INVESTIGATING THE POTENTIAL FOR TREATING WATER CONTAMINATED WITH TOLUENE USING ULTRAVIOLET-HYDROGEN PEROXIDE PROCESS

BY

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Dedication

To my family and friends…

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All praise and thanks is due to Allah; for it is by His Grace and Mercy that all things are possible.

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LIST OF ABBREVIATIONS

amu: Atomic mass unit

AOP: Advanced Oxidation Process

BTEX: Benzene, Toluene, Ethylbenzene, and Xylene

COD: Chemical Oxygen Demand

DBM: Diesel Base Mud

DIW: Deionized water

EPA: Environmental Protection Agency

GCMS: Gas Chromatography - Mass Spectrometry

GW: Groundwater

H_2O_2: Hydrogen peroxide

LP UV: Low Pressure Ultraviolet

MCL: Maximum Contaminant Level

MP UV: Medium Pressure Ultraviolet

NHE: Normal Hydrogen Electrode

OBM: Oil-Base Mud

OSHA: Occupational Safety and Health Administration

PAH: Polycyclic Aromatic Hydrocarbons

ppm: part per million

TDS: Total Dissolved Solids

TRE: Toluene Removal Efficiency

TWA: Time Weighted Average (8h/day)

VOCs Volatile Organic Compounds

WBM: Water Base Mud

ABSTRACT

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Improper disposal of diesel-based drilling fluids carries both health and environmental problems. Groundwater sources in an area with intense oil and gas exploration activities are highly susceptible to contamination with harmful ingredients of the diesel such as benzene, toluene, ethyl benzene and xylenes (BTEX). Removing these contaminants from contaminated water has been practiced with several techniques including adsorption, air stripping, chemical oxidation and biological degradation. Advanced oxidation processes (AOPs) are among the technologies that have also been tested and proved efficiency in removing contaminants from water but still require more studies to optimize the parameters for full mineralization. Therefore, this study aims to demonstrate the efficiency of UV/H_2O_2, as one of AOP processes, in remediating water contaminated with diesel-based fluids. Toluene was selected as the target pollutant due to its high solubility in water compared to other BTEX compounds. The study also aims to identify the optimum removal conditions of Toluene under various bench scale experimental conditions such as UV lamp type and intensity, H_2O_2 concentrations, pH, water salinity and contact time. Results of the study revealed that UV-H_2O_2 process has achieved 91% removal of Toluene in 10 minutes, and 97 % in 15 minutes in deionized water. In the study, pH 4, 100 ppm H_2O_2, and 15 Watt low pressure UV lamp were the best treatment conditions to remove 10 ppm Toluene from contaminated waters. Moreover, results showed that as salinity increases from 1250 ppm to 5000 ppm, the removal efficiency of Toluene decreases from 89% to 67% respectively at pH of 4 after 15 minutes contact time. Kinetics of the treatment process shows that the treatment follows a first-order kinetics with removal rate k = 0.3593.

ملخص الرسالة

الاسم الكامل: راكان حسن

عنوان الرسالة: دراسة امكانية معالجة المياه الملوثة بمادة التولوين بواسطة تقنية الأشعة فوق البنفسجية مع بروكسيد الهيدروجين

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التخلص غير السليم من سوائل الحفر التي تعمل بالديزل يتسبب في العديد من المشاكل الصحية والبيئية. على سبيل المثال فان مصادر المياه الجوفية في منطقة يوجد بها حركة نشطة في مجال التنقيب عن النفط والغاز هي عرضة للتلوث مع المكونات الضارة لسوائل الحفر مثل السولار والبنزين والتولوين والبنزين الإيثيلي والزيلين (BTEX). لقد تم تجربة العديد من التقنيات لإزالة هذه الملوثات من المياه الملوثة بما في ذلك الامتزاز، تجريد الهواء، والأكسدة الكيميائية والتحلل البيولوجي. عمليات الأكسدة المتقدمة هي من بين التقنيات التي تم اختبارها مؤخرا وأثبتت كفاءة في إزالة الملوثات من المياه ولكن لا تزال بحاجة إلى مزيد من الدراسات لتحسين ظروف المعالجة. ولذلك، تهدف هذه الدراسة إلى إثبات كفاءة تقنية استخدام الأشعة فوق البنفسجية مع بروكسيد الهيدروجين H_2O_2، باعتبارها واحدة من عمليات الأكسدة المتقدمة في تنقية المياه الملوثة بسوائل الحفر المحتوية على مادة الديزل. في هذه الدراسة تم اختيار مادة التولوين لتمثل مادة الديزل كونها الاعلى درجة ذوبانا في الماء بالمقارنة مع مركبات BTEX الأخرى. لقد هدفت الدراسة إلى تحديد ظروف العالجة المثلى لإزالة التولوين تحت ظروف تجريبية مختلفة كنوع وشدة الأشعة فوق البنفسجية وكثافة وتركيز مادة H_2O_2، ودرجة الحموضة وملوحة المياه والزمن اللازم للمعالجة. وكشفت نتائج الدراسة أن عملية الأشعة فوق البنفسجية H_2O_2 حقق إزالة 91٪ من التولوين في 10 دقائق، و 97٪ في 15 دقيقة من الماء المقطر. الرقم الهيدروجيني 4، 100 H_2O_2 جزء في المليون، و 15 واط من الأشعة فوق

البنفسجية كانت ظروف المعالجة الأمثل لإزالة 10 جزء في المليون من مادة التولوين. كما أظهرت النتائج أن ملوحة المياه تقلل من كفاءة تقنية استخدام الأشعة فوق البنفسجية مع بروكسيد الهيدروجين حيث انخفضت نسبة ازالة مادة التولوين من 89٪ إلى 67٪ عندما زادت درجة ملوحة المياه من 1250 جزء في المليون إلى 5000 جزء في المليون في درجة حموضة 4 خلال 15 دقيقة. ان تقنية المعالجة في هذه الدراسة كانت من الدرجة الأولى مع معدل إزالة حوالي 0.3593.

CHAPTER 1

INTRODUCTION

1.1 Background

1.1.1 Water Resources in Kingdom of Saudi Arabia

The Kingdom of Saudi Arabia is located in an arid region that suffers from the lack of fresh water resources. It depends primarily on desalination of seawater and non-renewable, limited groundwater resources for its potable water supply. With the increasing population in Saudi Arabia, local water authorities have dedicated intense efforts to search for new resources and to keep their water resources free from contamination. However, due to recent expansion of industrial activities, especially in the petrochemical and oil sector, contamination of water sources in general and groundwater specifically may be difficult to avoid.

One of the sources of contamination for water resources may come from hydrocarbons, including crude oil or its constituents like fuels or oily materials. In the oil industry, and specifically during drilling phases, many types of fluids are being used in drilling operations to help resolve drilling difficulties. The drilling fluids, also referred to as drilling mud, can be water base fluids or oil base fluids. Both systems are a mixture of materials that creates the target fluid properties suiting the place of usage. The oil-base mud (OBM) is used widely where the reservoir characteristics require its properties for

drilling success. In addition, water base mud (WBM) is usually replaced with OBM for operational reasons.

1.1.2 Oil-based drilling fluids

Oil-based drilling fluids or oil-based drilling muds (OBMs) are composed of two phases, an organic phase that consists of mineral oil, diesel, or low-toxicity linear olefins and paraffin, as well as an aqueous phase [1]. Moreover, to maintain a homogeneous mud system and thus achieve the proposed mud functions (i.e., good emulsion properties, rheology and carrying characteristics, and solid suspension), chemical additives, including emulsifiers, wetting agents, lime, fluid loss reducers, viscosities, and salts, must be used to reduce the aqueous phase activity.

The oil/water ratios, oil types (e.g., diesel, kerosene, or mineral oil), and chemical additives concentration differ from one region to another based on several factors. These factors includes, the environmental regulations for the oil type to be used, also the proposed mud properties suitable for drilling site conditions (formations, temperatures, pressures, etc.) [1, 59]. The general composition of the most common conventional oil-based fluids is a diesel type, due to its organic phase.

Oil-based fluids has some advantages over water-based, including stabilization, increased protection of water-sensitive formation, and higher lubricity. Diesel-based fluid is favorable among oils because of availability and cost, however in recent years new less

toxic alternatives with lower aromatic components and higher flash points in a form of highly refined mineral oils are replacing diesel based fluids, but still diesel is used [1].

1.1.3 Diesel

Petroleum based diesel is a liquid fuel that is obtained by fractional distillations of crude oil at temperatures of 200 °C – 350 °C and atmospheric pressure. Other form of diesel, like biodiesel, are obtained by other processes. Petro-diesel the most common type [2].

Diesel is composed of 75% saturated hydrocarbons (primarily paraffins) and 25% aromatic hydrocarbons, including naphthalenes, alkylbenzenes such as toluene, and polycyclic aromatic hydrocarbons (PAHs). The average molecular formula of diesel is $C_{12}H_{23}$ [3], [4].

Diesel has soluble hydrocarbons fractions, including benzene, toluene, ethylbenzene, and xylene (BTEX), that can partially dissolve into water. Thus, a recent study considered toluene as one of the parameters for analysis and as one of the indicators of diesel contamination in water when diesel spills occur [5].

1.1.4 Toluene

Toluene has a molecular formula of C_7H_8 with a molecular weight of 92.15 g/mol. It is a colorless, flammable, refractive liquid [6].

The highest weight percentage of BTEX components in diesel is 0.7% of the diesel weight [5]. Toluene is considered to be the major constitent among diesel water-soluble fractions of BTEX [7]. Toluene solubility in water is 0.561 g/L at 25ºC [8].

Toluene abundance within the diesel quantities used in diesel-based muds (DBM) is a considerable portion. Thus, toluene is a potential contaminant to water resources, including groundwater, and therefore is a main indicator of water contamination after a diesel spill event.

1.2 Diesel - Based Drilling Mud's Environmental & Health Risks

The usage of DBM as oil-based drilling fluids poses significant problems for wastewater remediation, and marine and groundwater. Water contamination with DBM can occur due to accidental spillage and leakage from drilling operations, specifically from activities like mud mixing areas, tanks, containers transportations, pipelines, and circulation loss at sub-surface activities.

The DBM risks to environmental degradation come from the toxicity that its petroleum hydrocarbons constituents (diesel) present to ecosystems. The hydrocarbon portion has a negative impact on the environment, including acting as a health hazard. These toxic materials can cause the imbalance of ecosystems and bioaccumulate within a food chain.

The DBM has toxicity as a fluid and as drilling cuttings produced from drilling debris, which presents difficulty in removing hydrocarbons contaminants by mechanical means. Consequently, the discharge of these cuttings is an environmental concern, beside the contamination that may occur from fluid spills or loss into the environment.

The adverse health effects of DBM on humans depends primarily on the concentration of diesel constituents introduced to the environment and can possibly be consumed by human. In other words, it depends on the dosage (length, frequency, and concentration of

exposure) in addition to the health of the person exposed. The health threats associated within a food chain or the consumptions of small amounts of petroleum hydrocarbons (diesel), specially the soluble parts such as toluene, over long periods of time through the drinking contaminated water can cause diseases and physiological malfunctions [9].

Regardless of the importance of the oil industry to the economy, the environmental challenges involved in oil production need to be assessed. Oil consists of aliphatic and aromatic compounds and the later are considered to be more toxic since they are more recalcitrant, like phenols [10].

Toluene can exist in the environment as a consequence of accidental events originating in industrial operational sites or relevant transportation. The exposure to toluene amount should not exceed the level that cause health harmful effects.

Toluene can be absorbed through the skin, eye contact, inhalation, or ingestion. The lowest published lethal dose for [Humans] via an oral route is 50 mg/kg. The toluene exposure limit, according Occupational Safety and Health Administration (OSHA), is 200 ppm Time Weighted Average (8 hours/day). Acute effects may cause headaches, drowsiness, and harm to lungs if swallowed. Severe exposure may cause respiratory problems, unconsciousness, seizures, and death. Chorionic effects can cause damage to the blood, kidneys, nervous system, liver, and brain. Toluene can also be detected in maternal milk in humans, indicating that other effects, including reproductive and birth shortcomings and genetic damages [8].

Environmentally, the short-term hazards of toluene can cause aquatic life toxicities, and confined areas are more affected. The long-term potential hazards of toluene include groundwater contamination, which occurs as a result of spills affecting potable (ground) water supply, and can cause chronic health problems resulting from exposure to aromatic compounds [11]. The drinking water maximum contaminant level (MCL) for toluene is 1 ppm, as proposed by the US environmental protection agency (EPA) [12].

1.3 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes (AOPs) are methods that have the capabilities to remove organic compounds that are not degradable by biological processes. AOPS involve remediation techniques for removing many organic pollutants from contaminated water. AOPs depend on the generation of a highly reactive species, i.e., super oxidants such as radicals rather than classical oxidants and mainly the hydroxyl radicals ($OH^{\bullet}$), to oxidize environmental contaminants.

AOPs are categorized by the release of hydroxyl radicals ($OH^{\bullet}$) that are a non-selective and highly reactive species employed to breakdown organic pollutants existing in soil and aquatic media -dissolved or dispersed- like wastewater.

Hydroxyl radicals ($OH^{\bullet}$) have high reduction potential (E_0 = 2.8 V), as shown in *Table 1* [13], and can react with many types of organic pollutants to achieve complete mineralization that can transform them to CO_2 and H_2O or decompose organic pollutants to a less toxic form [14].

Table 1. Standard reduction potentials (E0) of various oxidants in volts (V) compared with a normal hydrogen electrode (NHE, E0 = 0 V).

Oxidant	**Standard reduction potential (V vs. NHE)**
Fluorine (F_2)	3.03
Hydroxyl radical (•OH)	2.80
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.77
Potassium permanganate ($KMnO_4$)	1.67
Chlorine dioxide (ClO_2)	1.50
Chlorine (Cl_2)	1.36
Bromine (Br_2)	1.09

Many AOPs can generate or use various reactive species, including hydroxyl radical, according to C. P. Huang et al. [14]. In this study, a photochemical based AOP was generated that depended on light to generate hydroxyl radicals ($OH^{\bullet}$), specifically, using ultraviolet light with hydrogen peroxide (UV-H_2O_2) [15].

Hydroxyl radicals ($OH^{\bullet}$) have a high oxidation potential, which explains the reason why $OH^{\bullet}$-based oxidation processes have gained consideration for several AOP applications [15]. The results in *Table 2* indicate that the rate constant of $OH^{\bullet}$-based reactions are significantly higher than those using O_3 [16].

Table 2. Reaction rate constants (k, M^{-1} s^{-1}) of ozone vs. hydroxyl radical with organic compounds [15] [16].

Compound	***k* (M^{-1} s^{-1})**	
	O_3	$OH^{\bullet}$
Chlorinated alkenes	10^3 – 10	10^9 – 10^{11}
Phenols	10^3	10^9 – 10^{10}
N-containing organics	10 – $10^{}$	10^8 – 10^{10}
Aromatics	1 – 10^2	10^8 – 10^{10}
Ketones	1	10^9 – 10^{10}
Alcohols	10^{-2} – 1	10^5 – 10^9
Olefins	1 – 450 x	10^9 – 10^{11}
Acetylenes	50	10^5 – 10^9
Carboxylic acids	10^{-3} – 10	10^7 – 10^9
Sulfur-containing organics	10 – 1.6 x	10^9 – 10^{10}

1.4 Ultraviolet Light with Hydrogen Peroxide Process (UV-H_2O_2)

Hydroxyl radical ($OH^{\bullet}$) generation from H_2O_2 takes place through exposure to UV light that initiates the degradation process according to equation (1) [16].

$$H_2O_2 \xrightarrow{h\nu} 2HO^{\bullet} \quad \text{..... eq. (1)}$$

It has been shown that the increase of the initial concentration of H_2O_2 improves the mineralization rate of pollutants up to a maximum value. Thus, the rate begins to be reduced after reaching high H_2O_2 levels [17].

López et al. [18] explain that this decrease in the H_2O_2/UV treatment yield is due to hydroxyl radicals that react with excess H_2O_2, instead of reacting with organic compounds, leading to the formation of hydroperoxyl ($OH_2^{\bullet}$) that has reduction potential of 1.7 V, which less than the hydroxyl reduction potential as shown in equation (2).

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad \text{..... eq. (2)}$$

Produced hydroxyl radicals oxidize the organic substrates (RH), shown in the following equations (3 and 4) and due to the presence of hydroxyl radicals R• may undergo additional oxidation processes, yielding altered intermediates through various propagation and termination steps [19].

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \quad \text{..... eq. (3)}$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} + H_2O \rightarrow \text{further oxidation} \quad \text{..... eq. (4)}$$

Organic compounds will undergo various reaction routes upon oxidation with hydroxyl radicals, and if complete oxidation and degradation processes occurred, according the sum of equations of intermediates oxidation reactions, CO_2 will be produced as a final product, as shown in equation (5) [20], [21].

$$R\bullet + H_2O + O_2 \longrightarrow CO_2 + H_2O \quad \text{..... eq. (5)}$$

1.5 Significance of the Study

With the broad upstream oil industry and urbanization expansions in the country, the quality of limited groundwater resources is endangered by the risks of chemical pollution, especially from oil based drilling fluids' large production and widespread use of diesel, which is likely to be a present threat to groundwater resources.

From the above associated potential health impacts, these risks promote a pressing need to remove diesel contaminants, including toluene, from water and protect the groundwater resources from deteriorating in quality. Therefore, efficient, economic, and innovative water treatment techniques are needed to remove these contaminants.

AOP of UV-H_2O_2 demonstrated effective removal of organic contaminants in water, including fuels and volatile organic compounds (VOCs). However, little research has been carried out on the potential of AOPs to treat water contaminated with toluene. Therefore, this study aims to assess the potential of AOP using UV- H_2O_2 in removing toluene, as the target contaminant, from water under various treatment conditions.

1.6 Objectives

The main objective of this study is to assess the efficacy of advanced oxidation processes (AOPs) (UV - H_2O_2) in treating water contaminated with diesel-based drilling fluids at bench-scale levels. Toluene was selected as the target contaminant in this study. The specific objectives include:

1. Study the efficiency of the UV-H_2O_2 process for the removal of toluene spiked into water and determining the removal efficiency of toluene under various treatment conditions of UV lamps intensity, H_2O_2 concentrations, pH, Toluene concentrations, and contact time, in addition to defining any by-products

2. Assessing the kinetics of the treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Advanced Oxidation Process (AOP) for Diesel Contamination Treatment

Several AOPs used for diesel constituents removal from water have been reported. One example is Photo-Fenton, which appears to not be easily viable, because of the levels for ferrous ions disposal although wastewater containing diesel contamination achieved a total mineralization of 99%, while UV photolysis alone achieved 28% removal, and UV/H_2O_2, was able to mineralize 71%, with the results reported as total organic carbon (TOC) [22].

In another study, *in situ* experiments for sites contaminated with diesel were studied and a total petroleum hydrocarbon (TPH) removal of 63.5% was accomplished for contaminated soil by chemical oxidation using a 20% H_2O_2 solution [23].

The study conducted by Maha et al. [24] investigated AOP of Photo-Fenton for treating synthetic hydrocarbon wastewater generated by emulsifying diesel oil and water. The results reported a 70% removal as chemical oxygen demand (COD) after

120 min of treatment. However, the COD indicates the hydrocarbon removal without specification of the pollutants removed.

Morgana et al. [25] studied the removal of diesel from contaminated water by applying different AOPs of direct photolysis, peroxide, UV/H_2O_2, ozonation and O_3/UV. The results achieved by O_3/UV were the highest for maximum removal achieved in the shortest time, as shown in *Table 3*. These results showed that UV-H_2O_2 and O3-UV are efficient at removing diesel constituents at a rate of 95% and 96%, respectively. Several polynuclear aromatic hydrocarbon (PAH) by-products were detected, including naphthalene, phenanthrene, and alkyl-derivatives, which have adverse health impacts. Other by-product classes detected were phenols, ketones, ethers, and carboxylic acids. Morgana also concluded that publications regarding by-products are rare and, thus, the results are hard to compare.

Table 3. Removal efficiency over time for diesel degradation processes [25]

Process	Removal percentage / %	time / min
UV	75	60
UV/H_2O_2	95	105
H_2O_2	49	90
O_3	71	40
O_3/UV	96	30

Although previous studies did not solely focus on toluene or similar compounds, these reductions in TOC, TPH, COD may include toluene as a constituent of diesel, but there is not strong evidence without individual analysis. Understanding the individual degradation of diesel components and the resulting by-products formed is required.

2.2 Advanced Oxidation Processes for Toluene Removal

The AOP studies using UV- H_2O_2 for toluene removal are limited. Herein, a few examples are reviewed to allow comparison with the method implemented in this thesis.

The potentiality of AOP of TiO_2/UV, UV/ H_2O_2, Fenton, and Photo-Fenton was studied by the mineralization of aqueous solutions containing benzene, toluene, and xylenes (BTX) (E. R. L. Tiburtius, et al., 2005) [19]. In this study, the removal capability of the AOP for BTX removal was investigated, total phenol determination was used as a quantitative indicator, and the Photo-Fenton process showed the highest degradation rate for a phenolic compound that generated intermediates (more than 80% in 30 minutes) among other AOP. Thus, the Photo-Fenton process was selected for further experiments. The selected Photo-Fenton treatment presented almost a complete removal of 5 ppm toluene concentration in less than 20 minutes and a 75% removal of BTX in 90 minutes [19]. However the mineralization capacity, as determined by the response of BTX together as total phenol against the UV-H_2O_2 system, was not fully addressed. This study used only total phenol for intermediate degradation as a removal indicator. Also, a single set-up of 20 ppm BTX, 100 ppm H_2O_2 , and pH 6 required further investigation, and such investigations with different experimental set-ups showed the potential for toluene removal alone, under various conditions, and were required to elucidate the mechanism of toluene removal.

According to Katarína et al. [26], the removal of BTEX using O_3-H_2O_2 was investigated and the results showed the highest removal rate after 5 minutes, and

reached approximately 90% in 40 minutes. Toluene removal by this process was 68%, 76%, and 96% at 5, 20, and 60 minutes, respectively. Since this process showed a high efficiency for toluene removal, another techniques required to be studied to elucidate the most efficient AOPs for toluene removal, such as UV-H_2O_2 that is examined by this thesis.

Another study of Daifullah and Mohamed [27] used the UV-H_2O_2 system for degrading BTEX. The removal observed was >90% within 10 min of irradiation. This study used UV lamps at high pressure to emits 300 nm light with an intensity of 3.5 × 10−5 Ein L^{-1} min^{-1} that of 500 Watt power. This power is relativly high, and understanding the sufficient amount of UV irradiation power is crucial from an economical perspective. Therefore , studying diffferent UV irradiation is key and a focus in this thesis. Also, this study examined the removal at pH-3 only. pH variation is important to study for efficiency of removal and avoiding any addtion of supplementary chemicals for ph adjusting. Although the study showed good removal of BTEX, the by-products of toluene were not addressed.

The study by Mahmoud Bahmania et al. [28] reported BTEX removal using UV-H_2O_2 on a bench scale in water medium. BTEX removal under acidic conditions (pH 3) achieved 90% for 550 ppm and 98% for 210 ppm BTEX initial concentrations after 180 minutes of the treatment. It's obvious that removal time was higher than other reported studies and this could be due to the high initial concentration of BTEX. However, in this study COD was used to determine the hydrocarbon degradation for the pollutants mixture. Toluene and its by-products were not assessed and energy consumption was also not assessed.

Other studies showed different AOPs for toluene removal, specifically gaseous phase Ozone- photocatalysis processes (O_3-PCO) for toluene degradation were assessed. The toluene removal efficiency (TRE) showed good removal results, and since the mechanism of action of AOPs rely on OH• generation, these result can be considered provide insight into the toluene reaction. The O_3-PCO, UV/O_3, and O_3/TiO_2 TRE was 96%, 89.5%, and 86.5%, respectively [20]. Another gaseous phase study conducted by Yu and Lee [29] examined the carbon dioxide yields of TiO_2/UV and TiO_2/UV/O_3 processes. The study revealed that an improvement in CO_2 yield was noticed with increasing concentrations of toluene. A gap was detected between the total oxidation rate and CO_2 yield rates that improves with toluene concentrations; this indicates that some intermediates were not mineralized to CO_2 and H_2O within these techniques. Although these two studies examined toluene removal and showed removal occurrences, they used a different AOP than UV-H_2O_2, and both studies were conducted in gaseous medium. Therefore more investigation into aqueous medium and UV-H_2O_2 are required, which this thesis tries to address.

2.3 Effect of pH on Toluene Removal

Researchers have thoroughly studied the effect of pH on the removal of organic pollutants. The efficiency of AOPs is directly related to water quality parameters, such as pH for instance. The study by Vaferi et al. [28] concluded that alkaline pH and H_2O_2 concentration had opposite effects on the BTEX photodegradation using the UV-H_2O_2 process. The study by Mahmoud et al. [28] has similar observations when treating BTEX by the UV-H_2O_2 process.

PH value is a key influencer for the oxidation potential of ($OH^{\bullet}$) due to the reciprocal relation of the oxidation potential to the pH value. PH significance affects ($OH^{\bullet}$) generation and consequently the oxidation efficiency. It has been observed that when the photo-Fenton and photo Fenton-like processes used for treating industrial wastewater were contaminated with hydrocarbons, the removal rate decreased when the pH increased [30].

From the above observations, it can be understood that pH factor is important during removal of toluene using UV-H_2O_2. Experiments assessing this assumption were conducted within this study.

2.4 Effect of Initial Toluene Concentrations on Toluene Removal

Toluene removal from 1.0–20 ppm concentrations in the gas-phase were investigated. The breakdown of low-level gaseous toluene during O_3/UV treatment is greatly influenced by inlet concentration. The degradation of toluene at low levels gradually decreased with increasing inlet concentration during TiO_2/UV and O_3/TiO_2/UV treatments [31]. Thus, we can conclude that toluene concentration is a factor that need to be considered when designing experiments using UV-H_2O_2 to remove toluene.

2.5 Effect of UV Light Intensity on Toluene Removal

UV light intensity has been shown to influence the efficiency of toluene removal when using UV-H_2O_2 when a medium pressure lamp was used for BTX removal [19]. In

order to study the influence of UV light wavelength on the degradation of toluene by O_3/UV, TiO_2/UV and O_3/TiO_2/UV in gaseous-phase treatments under these conditions showed that the degradation during irradiation with a 254 nm UV lamp was much greater than that at 365 nm. The substantial differences can mainly be explained due to the intensity of the light, since the 254 nm lamp irradiates a stronger UV intensity (about 58 W/m^2) than that of a 365 nm lamp, which irradiates at 30 W/m^2 according to Pengyi et al. [31]. This factor must be considered while optimizing conditions for toluene removal using UV-H_2O_2.

2.6 $OH^{\bullet}$ as an Oxidant for Toluene Removal

Most of AOPs use the hydroxyl radical as an oxidant for removal of organic pollutants. One study (H. Huang and W. Li, 2011) [20] suggested a mechanism of action where OH• was abundantly made by the UV-TiO_2, O_3-TiO_2, UV-O_3, and O_3-electron–hole pair treatments against toluene degradation. The suggested mechanism is shown in Figure 1, which cannot completely describe the degradation of toluene because of a lack of irrefutable proof and that it is very difficult, due to presence of several minor pathways. Also, due to the high reactivity of radical intermediates, detection is complicated.

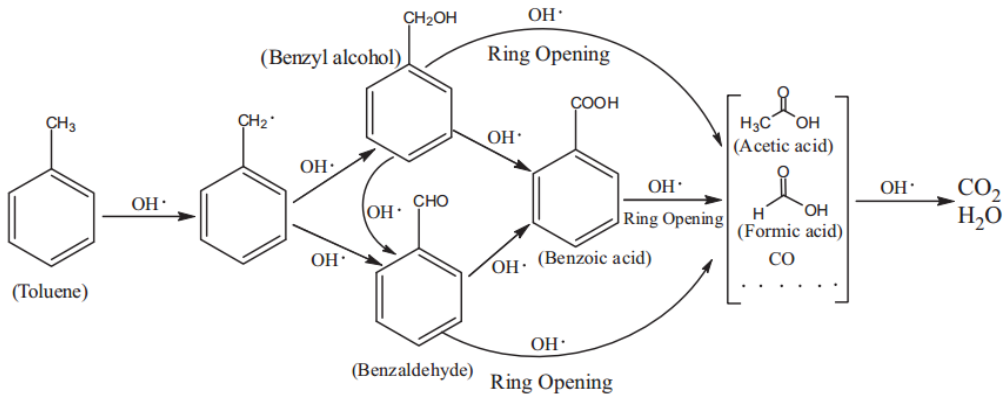

Figure 1. Hydroxyl radical (OH•) as oxidants

The main toluene oxidation pathway by OH• involves H-abstraction from the methyl group, producing a benzyl radical, and followed by creation of benzyl alcohol and/or benzaldehyde. Both can be attacked by an OH•, resulting in benzoic acid. Benzaldehyde, benzoic acid, and benzyl alcohol can be further attacked by OH•, leading to an aromatic ring opening, as suggested in Figure 1. After the ring opening, the generated compounds have a smaller molecular mass, such as formic acid, acetic acid, and CO_2. Such reactions can be affected by the sequence of OH• attack, resulting in the creation of non-harmful carbon dioxide and water molecules [20], [32]. All products after ring opening are more volatile than toluene, and thus are expected to start evaporating before being converted to CO_2.

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Chemicals

Toluene (analytical grade at 99.95% assay purity) was supplied by AJAX Chemicals, (Auburn) Australia. Hydrogen peroxide solution (30% w/w) was supplied by Scharlau®, (Sentmenat) Spain. Acetic acid (99.7% assay purity) was supplied by Fisher Scientific, (New Jersey), USA. Na_2CO_3 (≥ 99.5% purity) was supplied by Panreac®, (Barcelona), Spain. Sodium thiosulfate (≥ 98% purity) was supplied by Sigma-Aldrich (Steinheim) Germany. Benzaldehyde (> 99% purity) was supplied by MERCK- Schuchardt Germany.

3.1.2 Instrumentation

3.1.2.1 The Bench-Scale Photoreactor

A NORMAG® tabular photoreactor with forced liquid circulation was used for this study, as shown Figure 2. The photoreactor fixed on a tripod frame table was developed with powder-coated tube connectors. The reactor vessel had a total volume of 500 mL. The system consisted of the following compartments: radiation vessel with tempering mantis, cooling tube, immersion tube, circulation pump (Hostaflon®), splash-proof

guided counter magnet with a flanged driving motor, control unit for the driving motor, threaded tube connection, connecting piece for a fumigation frit with a spherical ground joint cup and cock, screwed clip, hose connector couplings, clips for spherical ground joint, and a thermometer.

The reactor has a fully Hostaflon® coated pump rotor. The liquid above the pump is sucked down, thrown outwards by the pump rotor, forced up through the riser pipe, and fed back to the reaction chamber through the upper end of the pipe.

Two types of UV lamps were used in the study. These are low pressure and meduim pressure lamps and both were obtained from Heraeus (www.heraeus-noblelight.com). As per the manufacturer, the two lamps operate at the following wavelength ranges. The low pressure (LP) emits radiation at a wavelength of 245 nm with an intensity of 15 Watts (TNN 15/32. 55 Volts, Cat No. SAA 09370) and the medium pressure lamp (MP) delivers a broadband spectrum over the complete range of 200-300 nm with intensity of 150 Watts (TQ 150, 85 Volts, Cat No. SAA 09360).

The emission spectra of the two lamps (15 Watts LP and 150 Watts MP UV lamps) are different, as shown in Figure 3 and Figure 4. As per the manufacturer of the UV lamps, the LP lamp produce a spectrum of radiation that is mainly at 254 nm and can be described as practically monochromatic since the other lines are in the UV and visible regions radiate very faintly in comparison to the 254 nm line. The MP lamp emits light from a 150 Watts power source mercury lamp and emits a wide broadband, extending from the short-wave UV range of approximately 240 nm to the visible region. Within this range, there are several intense bands and a number of weaker lines. In fact, it was shown that the MP lamp of the photo-reactor (150 Watts) give much weaker intensity at

the 254 nm wavelength but it has significant UV peaks at higher wavelengths, including 365 nm. It also emits very strong peaks within the visible region.

The radiation or light intensity emitted by the LP and MP UV lamps were calculated as $6.5*10^{-3}$ mW/cm^2 and $53*10^{-2}$ W/cm^2 **,** respectively [31], [33].

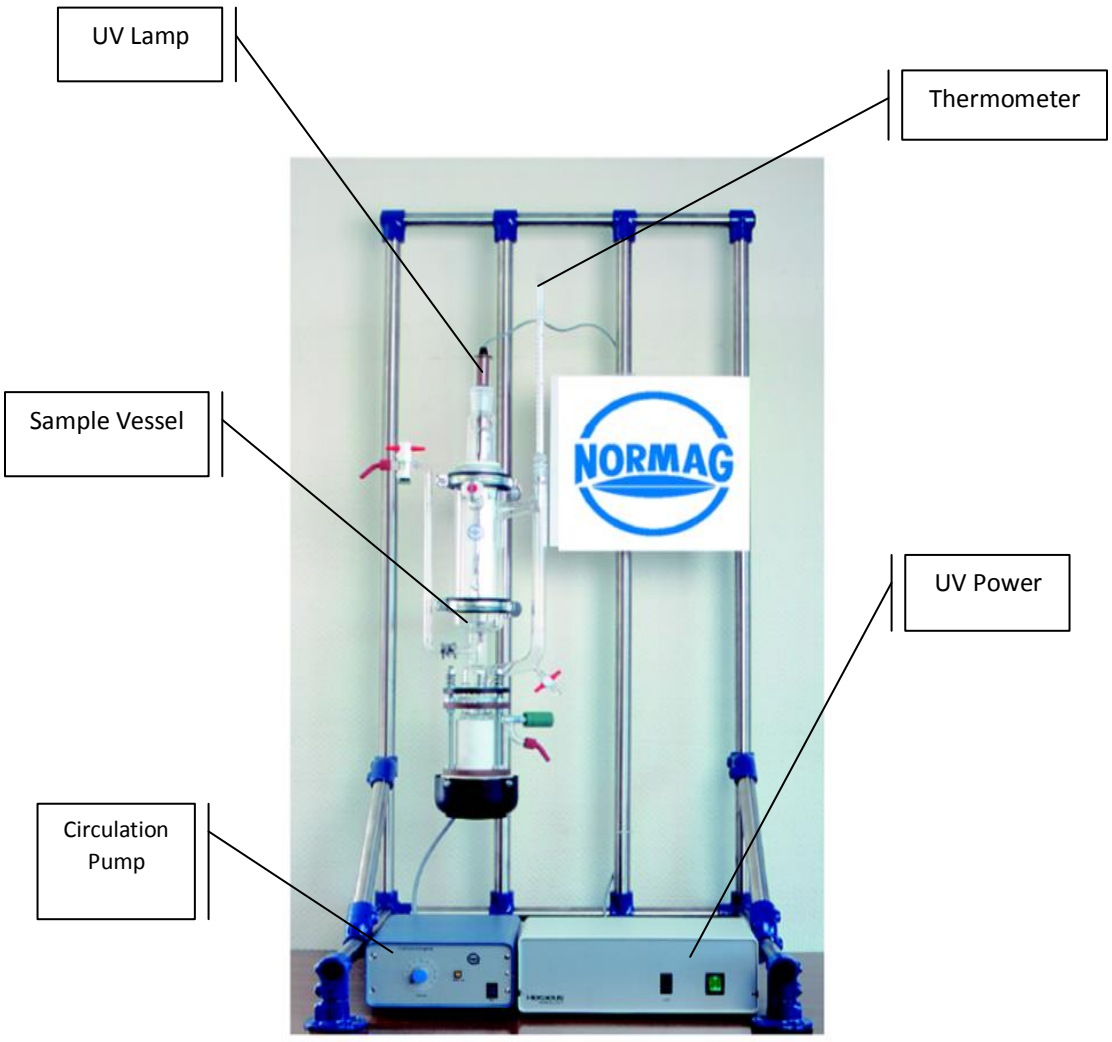

Figure 2. The Bench-Scale UV Photoreactor

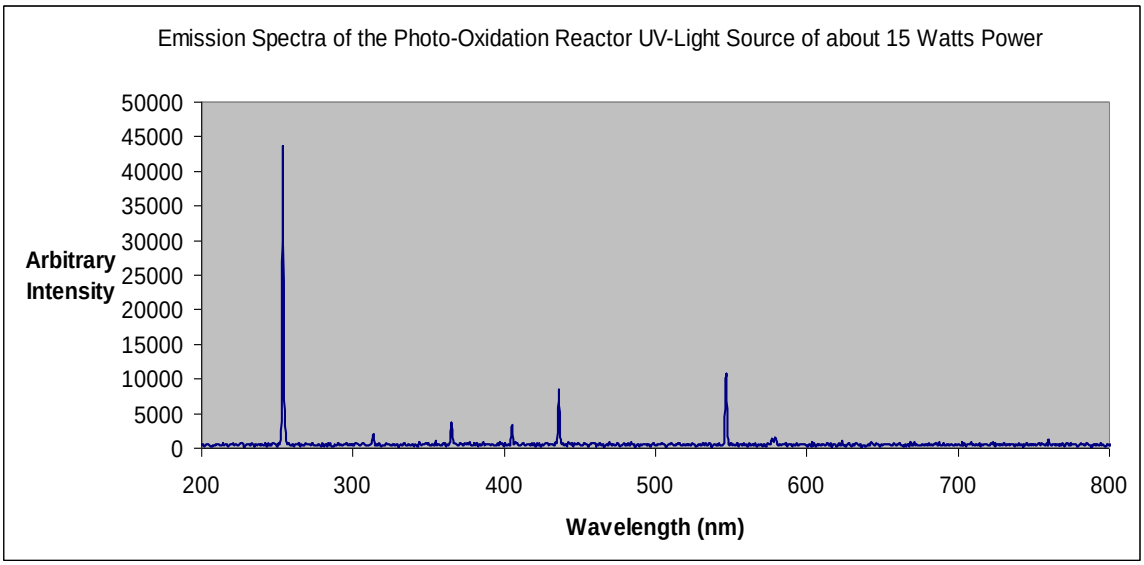

Figure 3. Emission spectra of the low pressure 15 Watt UV-Light

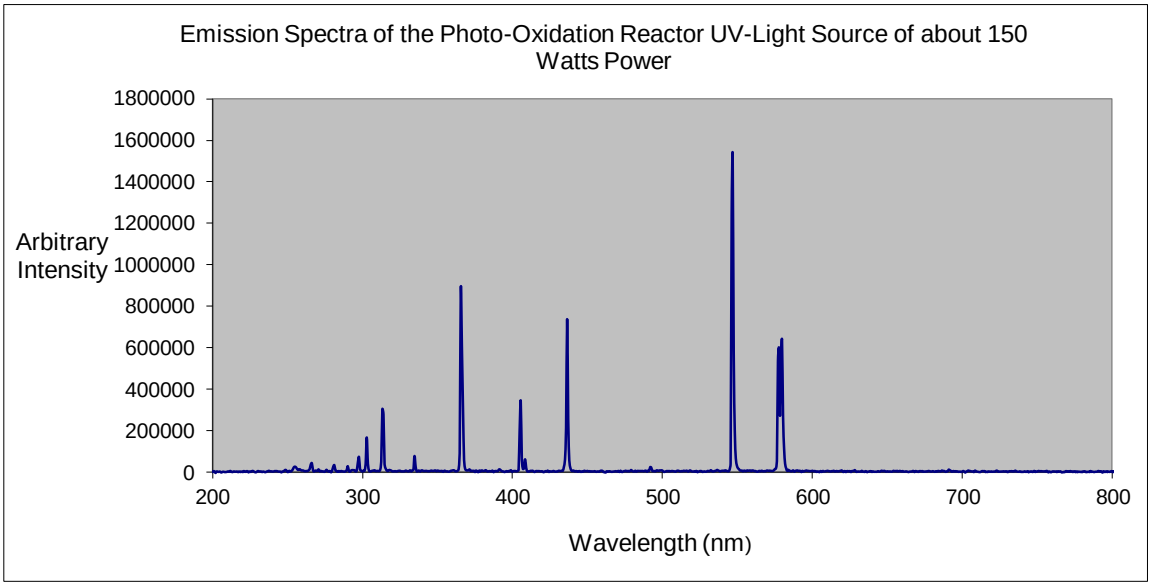

Figure 4. Emission spectra of the medium pressure 150 Watt UV-Light

3.1.2.2 Gas Chromatography/Mass Spectrometry (GC-MS) System

A 5890N Agilent GC coupled with an Agilent 5973 ISQ single quadrupole mass spectrometer (MS) and combined with an Agilent 7683 injector (Fig. 5) was used for the analysis of toluene and its by-products. A J&W GC DB5 capillary column containing the SE-54 phenyl-methyl stationary phase with a 60 meter length, 0.255 mm ID , and 0.25 μm film thickness was used.

Samples were introduced to the GC via the injector and a 2μL syringe; the injector is electronically connected to the GC-MS system. The GC-MS analysis method used was EPA 8260A. The carrier gas was helium in the constant flow mode at 1.2 mL/min and n a average velocity of 28 cm/sec. The oven temperature was programmed to 40 ºC, following which it was ramped at a rate of 8 ºC/minute to 100 ºC and then increased to 200 ºC at a ramp rate of 30 ºC/minute. The injection temperature was 250 ºC and the sample was injected using the splitless mode. The syringe temperature was set at room temperature. The mass transfer line of the mass spectrometer was kept at 280 ºC, while the ion source was 230 ºC. Election ionization (EI) mode was used for analysis. The set range mass for toluene was 92 amu. Selected ion monitoring (SIM) was used to acquire the ion current at only the mass to charge ratio values of interest, thus increasing the instrument's sensitivity. 10 mL of collected water sample was extracted from 22 ml of sample obtained during the experiment. This was then portion of that 10 mL transferred to the injector by a 2 μL syringe for analysis. The GC-MS output was acquired, stored, and processed by the GC using the MS library data base from Agilent technologies (ChemStation).

Fig. 5. Agilent GC-MS 5890N Model

3.1.2.3 UV-VIS Spectrophotometer

An Analytik Jena's UV-VIS spectrophotometer SPECORD® 50 (Fig. 6) was used to monitoring toluene and its residual by-products during treatment. The system was connected to a desktop computer that has the WinASPECT® PLUS operating software. The system was turned on 30 minutes to warm up the lamp before use. The UV light in the visible range was emitted from a halogen lamp. The selected light spectrum (262 nm) was filtered through the entrance slit and reflected back after irradiation on a concave grating mirror, then passed through the exit slit to reach the quartz coated mirror. The second cuts coated plane mirror reflected the selected light of the spectrum to the sample compartment, and then the light spectrum passed through the cuvette containing the sample. The absorbance was obtained from the detector. The quartz cuvette provided with the system was used to place the sample in the sample compartment. From the two detector signals, the measuring system of the

SPECORD® 50 established the photometric results. This means that changes of the single-beam signal, due to variations in the light yield of the source, are compensated for.

Fig. 6. Analytik Jena SPECORD® 50 UV-VIS Spectrophotometer.

3.2 Methods

3.2.1 Preparation of Stock Solutions

3.2.1.1 Preparation of Toluene Stock Solution

To prepare a 100 ppm toluene stock solution in 500 mL, 295 µL of pure toluene of 99.95% assay purity was placed in a clean and dry 500 mL volumetric flask, the flask filled to the mark with deionized water (DIW), and then tightly closed immediately. The toluene spiked DIW was stirred continuously for 30 minute until the toluene completely dissolved in the water. The desired concentration of toluene was diluted

into another 500 mL volumetric flasks from this stock solutions into 5, 10, and 15 ppm solutions. Freshly prepared stock solutions were prepared daily.

3.2.1.2 Preparation of Hydrogen Peroxide (H_2O_2) Stock Solution

A H_2O_2 stock solution of 1000 ppm concentration was prepared by transferring 302 µL of 30% w/w pure hydrogen peroxide solution into 100 mL of deionized water (DIW), which was then stirred for 15 minutes to assure homogeneity. Subsequent concentrations of 50, 100, and 200 ppm were prepared by dilution.

3.2.1.3 Preparation of Benzaldehyde Stock Solution

A Benzaldehyde stock solution of 1000 ppm concentration was prepared by transferring 95.7 µL of pure benzaldehyde (>99%) into 100 mL of deionized water (DIW). The mixture was then stirred for 15 minutes to assure homogeneity. Subsequent concentrations of 10 ppm were prepared by dilution.

3.2.2 Instrument Calibration

3.2.2.1 Calibration of GC-MS

A stock solution of toluene (100 ppm) was prepared in the laboratory by adding calculated amounts of toluene to water and stirring for 30 minutes. Then, for the quantitation, several dilutions were prepared for 5 points of concentrations (400, 500,

1000, 2400, and 4000 ppb) and injected in the GC-MS to make the calibration curve. A representative toluene calibration curve is shown in Figure 7.

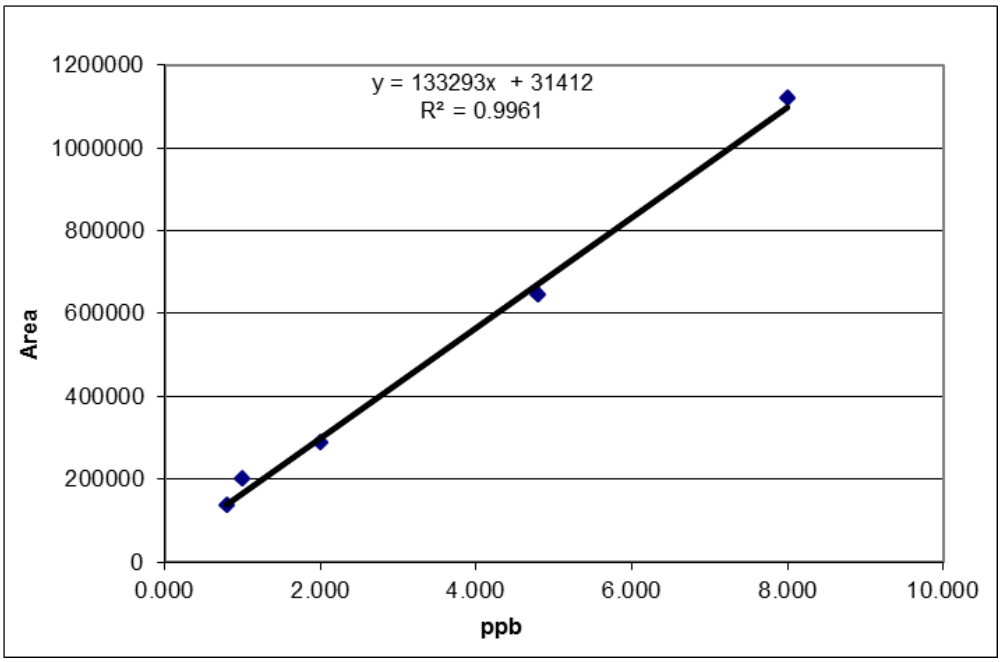

Figure 7. GC-MS calibration curve for toluene

Another calibration curve was created for benzaldehyde. A 100 ppm stock standard solutions of benzaldehyde was prepared in the laboratory and stirred for 15 minutes. Then, for the quantitation, several dilutions made for 4 points of concentrations (5, 50, 200, and 1000 ppb) and injected into the GC-MS to create the calibration curve. A representative benzaldehyde calibration curve is shown in Figure 8.

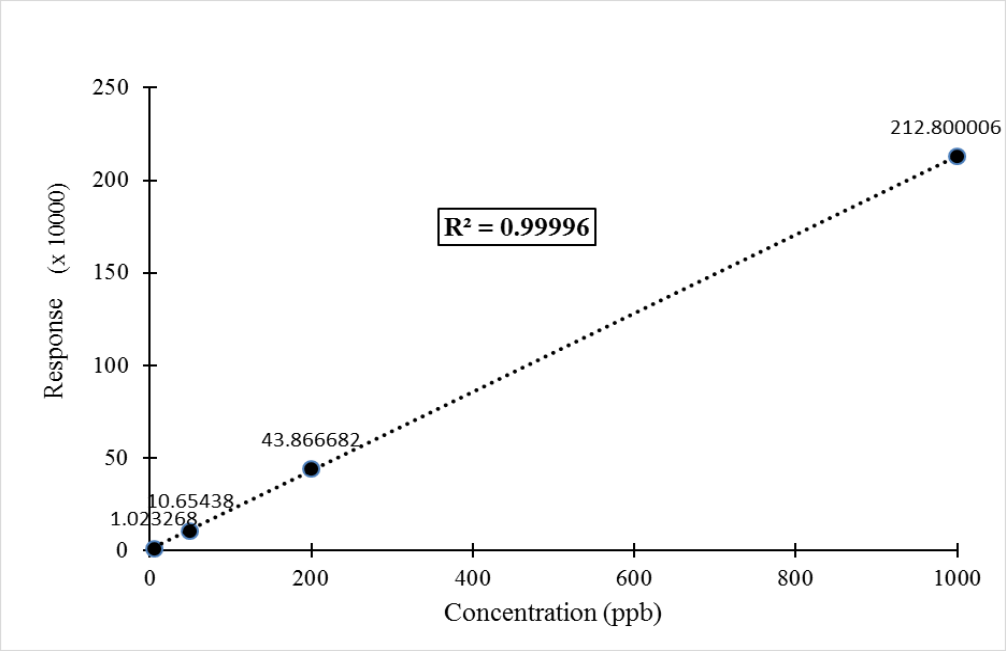

Figure 8. Calibration curve for benzaldehyde

3.2.2.2 GC-MS Sample Preparation Method

A 2 mL water sample from a 40 mL collected sample in a glass bottle was extracted vigorously with 10 mL dichloromethane (DCM). After 1 hour, the DCM-extract was collected in a 2 mL vial for analysis. A sample of 2 µL was injected onto the GC-MS for toluene analysis. This preparation was in accordance with EPA method 3510c for separatory funnel liquid-liquid extraction.

3.2.2.3 Calibration of UV-VIS Spectrophotometer

The UV-VIS Spectrophotometer instrument was calibrated before use. Prior to calibration, scanning of toluene solution in the UV-VIS range of 180 to 500 nm revealed that the highest λ_{max} occurred at 262 nm. As shown in Figure 9.

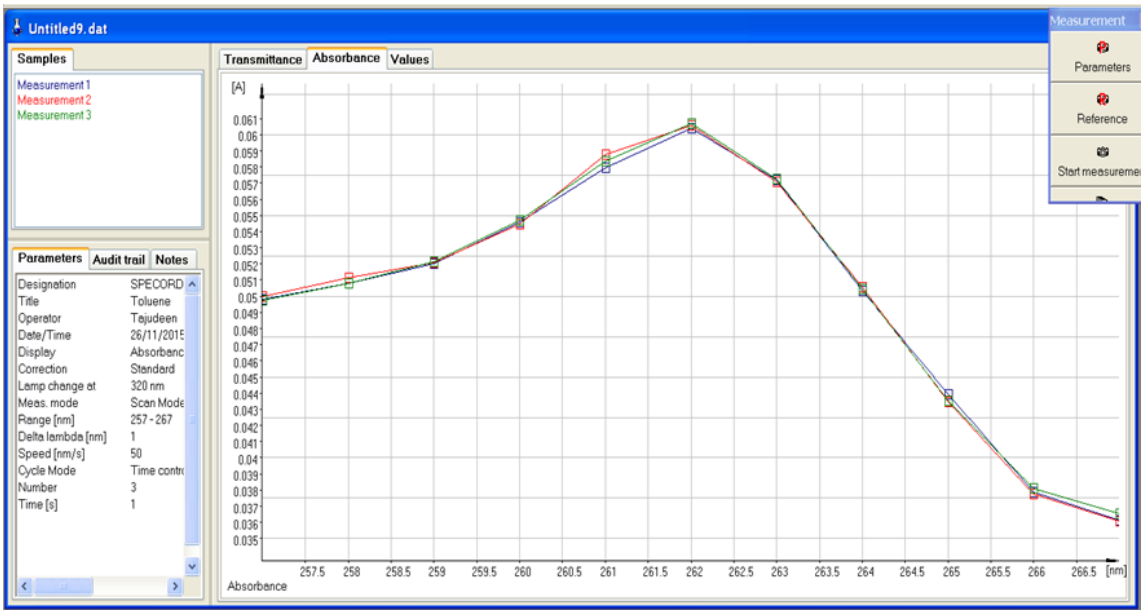

Figure 9. A fraction of UV spectrum for toluene showing the λ_{max} at 262 nm

Six working standard solutions at various toluene concentrations (0.5, 1, 5, 10, 15, and 20 ppm) were used during instrumental calibration and each standard was run in triplicate to minimize error. The straight line calibration curve obtained has a correlation coefficient (R^2 value) of 0.9839, as shown in Figure 10.

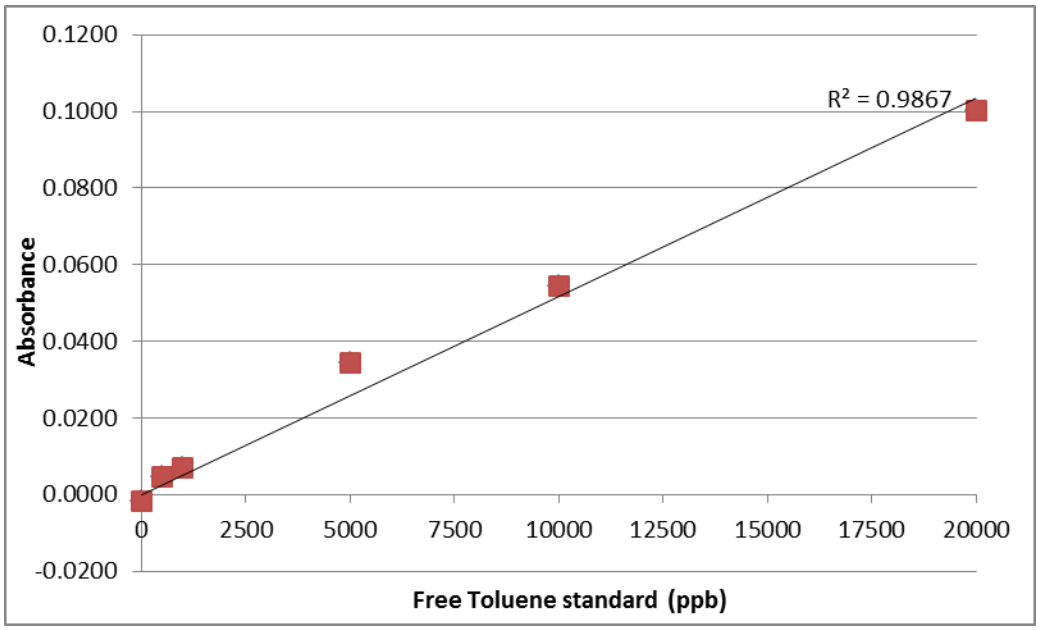

Figure 10. UV-Vis spectrophotometer calibration curve for toluene

3.2.3 Experimental Procedures

A bench-scale experimental study was conducted using a photo-reactor running in batch mode. The reactor unit has volume of 500 mL and housed low pressure and medium pressure UV lamps. Water bath circulation was activated to maintain a constant water temperature in the main vessel when the UV lamps were in operation.

Different experimental factors (e.g. stirring speed, H_2O_2 concentrations, UV lamps intensity, toluene concentration, salinity, contact time, and pH) and their influence on the efficiency of removal of toluene were assessed. The following general experimental procedures were followed:

Approximately 500 mL of DIW spiked with the desired toluene concentration (10 ppm) was transferred into the reactor vessel through the sample feeding inlet.

Before starting the actual treatment, the water spiked with toluene was stirred for 5 minutes to ensure a uniform distribution of toluene before collection of the first sample. The circulation pump was set up at a constant rate (50% of pump capacity).

The cold water hose from the circulating water bath was connected to the inlet of the photoreactor vacuum between the lamp house and reactor, and to the outlet. The cold water helped to maintain the temperature of the water in the reactor between 22-26 ºC during MP UV operation.

When H_2O_2 was used in the treatment run, certain concentrations of H_2O_2 (50, 100, and 200 ppm) were added to the water spiked with toluene while circulating.

When UV irradiation is used, a selected type of UV lamp (either 15 Watts LP or 150 Watts MP) alone or with H_2O_2 was used to illuminate the spiked water samples during circulation.

When UV irradiation and H_2O_2 are used together, first the desired concentration of toluene was injected as mentioned, followed by H_2O_2 addition, and then the selected lamp illuminated the circulating water. Samples were collected during each treatment run at various time intervals (0, 15, 30, 34, 60 min) and analyzed.

When UV, H_2O_2, or UV- H_2O_2 was used, the sample vials for GC-MS were dark glass and contained sodium thiosulfate to retard the reaction during the holding time. Samples were refrigerated until the samples were analyzed.

Various treatment runs were conducted at various combinations of UV, H_2O_2, pH, toluene concentration, and time interval to obtain the optimum treatment conditions for toluene removal, in addition to determine the kinetics of the reaction.

The specific procedures for different treatment conditions are presented in the following sections, followed by experiments 'layout in Table 4.

3.2.3.1 Blank Runs

a) 500 mL of DIW spiked with toluene was placed into the photoreactor vessel.
b) Toluene residual in the collected water samples were measured at 0, 15, 30, 45, and 60 min.

3.2.3.2 Stirring Runs

a) 500 mL of DIW spiked with toluene was placed into the photoreactor vessel
b) Toluene residuals of stirred and spiked water samples were collected and measured at 0, 15, 30, 45, and 60 min.

3.2.3.3 Treatment with Hydrogen Peroxide Alone

a) The desired concentration levels of H_2O_2 from the prepared stock solution were added to the photoreactor vessel that contained toluene spiked DIW.
b) Samples were collected at 0, 15, 30, 45, 60 min and measured for residual toluene.

3.2.3.4 Treatment with UV Exposure Alone

a) Temperature of the photoreactor vessel was adjusted by using the water bath circulation system.

b) 500 mL of DIW spiked with toluene was placed into the photoreactor vessel

c) Toluene spiked water samples were irradiated by the UV lamps: 15 Watt LP or 150 Watt MP.

d) Samples were collected at 0, 15, 30, 45, 60 min and measured for residual toluene.

3.2.3.5 Treatment with UV- H_2O_2 Process

a) Temperature of the photoreactor vessel adjusted.

b) The desired concentration levels of H_2O_2 were added to the photoreactor vessel that contained toluene spiked DIW.

c) Toluene spiked water samples with added H_2O_2 were irradiated by the UV lamps: 15 Watt LP or 150 Watt MP.

d) Samples were collected at 0, 15, 30, 45, 60 min and measured for residual toluene.

Table 4. Experimental layout

Treatment	Experimental parameters						
	Toluene C_i (ppm)	Stirring speed (% pump capacity)	pH	H_2O_2 dose (ppm)	UV type	TDS	Treatment time (min)
Blank	10	-	7	-	-	0	60
Stirring	10	(25- 50)	7	-	-	0	60
H_2O_2 alone	10	50	7	(20-50-100)	-	0	60
UV alone	10	50	7	100	(LP-MP)	0	60
UV- H_2O_2	(5-10-15)	50	7	100	LP	0	60
UV- H_2O_2	10	50	7	(50-100-200)	LP	0	60
UV- H_2O_2	10	50	(4-7-9)	100	LP	0	60
UV- H_2O_2	10	50	7	100	LP	GW% (25-50-100)	60

3.2.4 Kinetic Study

The kinetic studies were conducted for selected treatment results. The kinetic studies were carried out for toluene removal, and are best described by a first degree equation using [- ln (C/C_0)] vs time.

Where C is the final concentration and C_0 is the initial concentration, and the log (Y axis) is plotted over time (X axis).

3.2.5 Estimation of Electrical Energy per Order (EE/O)

(EE/O) is used as an appropriate figure-of-merit to estimate the required energy in kWh/m^3 to degrade 90% of the low concentration organic pollutants in water and wastewater. This technique has been proposed by the Photochemistry Commission of the International Union of Pure and Applied Chemistry, who also recently proposed a figure of merit for AOTs [34]. The electrical energy needed to degrade one order of toluene using different advanced oxidation process was presented as the UV dose using batch mode. The following equation was used to estimate EE/O:

[UV dose (kWh/m^3) = UV power (kW) x Time (hr) / batch reactor volume (m^3)]

According to the Calgon Corporation Handbook on Advanced Oxidation Technologies [35], the unit conversion factor liter to m^3 is L/1000, and for time is 1/60. The unit of EE/O is kilowatt-hours (kWh/m^3).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Identifying Toluene Removal in Deionized Water

In the following sub-sections, the results of toluene removal from water conducted at bench scale are presented. The study was conducted under different experimental conditions, including H_2O_2 dose, UV LP/MP, UV- H_2O_2, and time. A synthetic water sample was prepared by spiking a known concentrations of toluene in DIW and subjecting this solution to treatment under selected treatment conditions. Samples were analyzed by UV-Vis spectrophotometry for removal of the combined toluene and by products and also by GC-MS for toluene removal only. The raw groundwater was also spiked with toluene to test the optimized treatment conditions under authentic environmental conditions. The results are compared with those reported.

4.1.1 Removal of Toluene by Stirring Only (Blank Runs)

Blanks runs were conducted to estimate the loss of toluene due to stirring. In these experiments no H_2O_2 was added and experiments were also conducted in absence of UV light, 10 ppm of toluene was spiked into DIW, and continuously circulated for 60 minutes at constant flow rates (0, 25, and 50% of pump capacity) in the closed system photoreactor. The results shown in Figure 11 indicate that there is no loss of toluene

after stirring for 60 minutes. During a blank run at a zero stirring pump rate, a 3.4% decrease of toluene observed, and at a 25% of pump capacity no loss observed. Meanwhile, at a 50% of pump capacity the decrease was 8.7%. The decrease due to the volatilization behavior of toluene is very weak. There was no degradation of toluene due to circulation alone, which was confirmed by these experiments. In summary, blank runs showed that toluene solutions are relatively stable and no removal of toluene is expected to take place due to the effect of stirring. In conclusion. No loss is observed and any loss was due to experimental error.

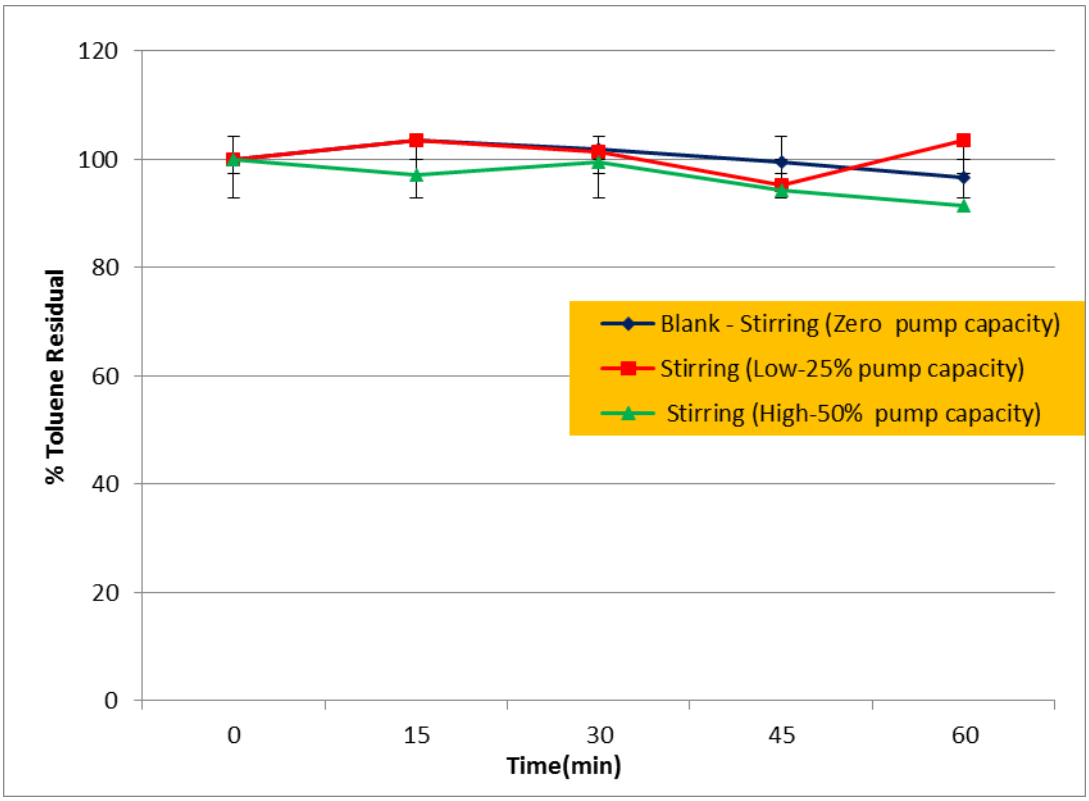

Figure 11. Residual toluene after continuous circulation for 60 minutes at 10 ppm initial toluene concentration

4.1.2 Removal of Toluene by H_2O_2 Alone

Several treatment runs were carried out to explore the effect of H_2O_2 doses on toluene removal. In these experiments, hydrogen peroxide doses of 20, 50, and 100 ppm were used to remove 10 ppm toluene from spiked water. Samples were collected over 60 minutes contact time at different intervals (0, 15, 30, 45, and 60 min). Figure 12 shows the results of residual toluene with the three doses of hydrogen peroxide alone. The results revealed that no significance loss of toluene is observed after 60 minutes of incubation in 20, 50 or 100 ppm of H_2O_2. Respectively, 1.3%, 8.2%, and 1% toluene decrease were observed. Similar to the stirring experiments, there were no appreciable removal of toluene. The results of three doses did not show a decrease in percentage for Toluene higher than 8.7%, which was the maximum obtained by stirring loss. Out of the three hydrogen peroxide dosages tested, it can be concluded that H_2O_2 alone is not effective for toluene removal, even with highest dose used. Of course, hydrogen peroxide must be broken down into OH• radicals for it to be effective oxidant [36]. Absence of UV light implies inefficient hydrolysis of H_2O_2 [14].

H_2O_2 is a common reactive oxygen species that decomposes to water and molecular oxygen. H_2O_2 is non-selective electrophilic oxidant with reduction potential of E° = 1.77 V with a normal hydrogen electrode (NHE, E° = 0 V) and it is a weak oxidant under mild conditions [37]. Therefore, it can be stated that the target pollutant toluene requires a stronger oxidant, such as OH• radical that has reduction potential of 2.80 V vs. NHE.

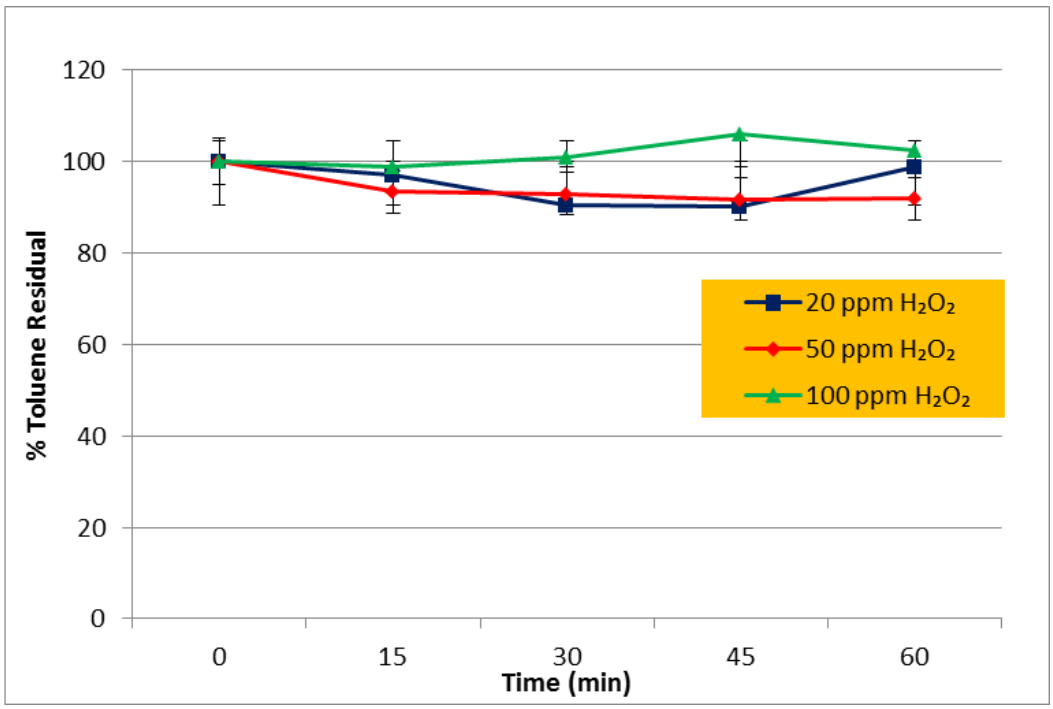

Figure 12. Residual toluene after treatment with 20, 50, and 100 ppm of H_2O_2, 10 ppm initial toluene concentration, and 60 minutes contact time.

4.1.3 Removal of Toluene by UV Alone

The effect of UV irradiation was investigated for the photolysis of toluene by a 15 Watts low pressure (LP) UV lamp with the intensity of $6*10^{-3}$ mW/cm^2 and by a 150 Watts medium pressure (MP) UV lamp with the intensity of $5.3*10^{-2}$ W/cm^2. These experiments were conducted using 10 ppm toluene spiked water samples that were exposed to the mentioned irradiation UV lamps. Water samples were collected after irradiation for different time intervals (up to 60 minutes treatment) and analyzed. The results showed an increase in the UV-Vis spectrophotometer reading at λ_{max} of 262 nm, reaching around 300% of the original toluene concentration after 45 minutes, for (LP) UV lamp and 250% after 30 minutes for the (MP) UV lamp. Both declined after that time, as shown in Figure 13 which demonstrates the residual toluene & by-products after irradiation by the (LP) and (MP) UV lamps. These results indicate that the photolysis reaction that degrades toluene took place to form other molecules that have stronger absorbance than toluene at 262 nm upon exposure to UV irradiation. These compounds have higher absorbance because they have a chromophore involving C=O bonds in conjugation with benzene and thereby exhibiting a higher absorbance than toluene [32], [38]. Example of these compounds include benzaldehyde and benzyl alcohol.

Photolysis of organic compounds occurs when compounds absorb the photons from irradiation and become energized and excited in the presence of oxygen or water, and then are decomposed as result of oxidation [39]. Apparently toluene undergoes photolysis by the two UV lamps' light, and the formed by-product strongly absorbs light at the 262 nm wavelength, much more than toluene alone.

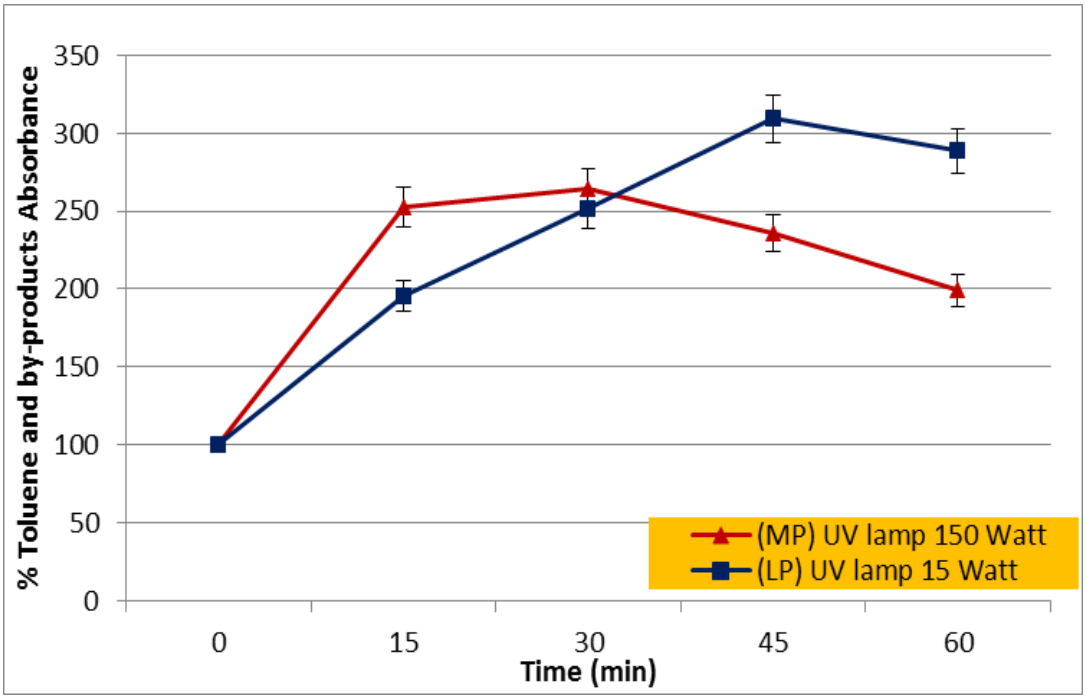

Figure 13. Toluene and by-products absorbance after treatment with LP and MP UV lamps, 10 ppm initial toluene concentration, and 60 minutes contact time.

In an effort to identify some of the toluene by-products, the experiment was repeated and samples were collected and analyzed by GC-MS. The GC-MS spectra showed two main components in the solution, toluene and benzaldehyde. The results are presented in Figure 14 for both the LP and MP UV lamps. Results show that residual toluene removal (94.5%) is accomplished after 60 minutes treatment for the LP UV lamp, and 94% removal was achieved for the MP UV lamp. Comparing both UV intensity lamps results indicates that the MP lamp achieved a more rapid removal of toluene at 15 and 30 minutes of contact time by 18%, compared to the LP lamp. From Figure 14 as can be seen that UV irradiation contributes to toluene treatment, unlike hydrogen peroxide alone. This is because UV irradiation can help generation of OH• radicals that eventually oxidize toluene very slowly [40]. Similar observations have been reported by M. Bahmani et al. [41] for benzene, toluene, ethylbenzene and xylene (BTEX) using UV lamps alone. Similarly, they reported that increasing the number of UV lamps increases the removal rate.

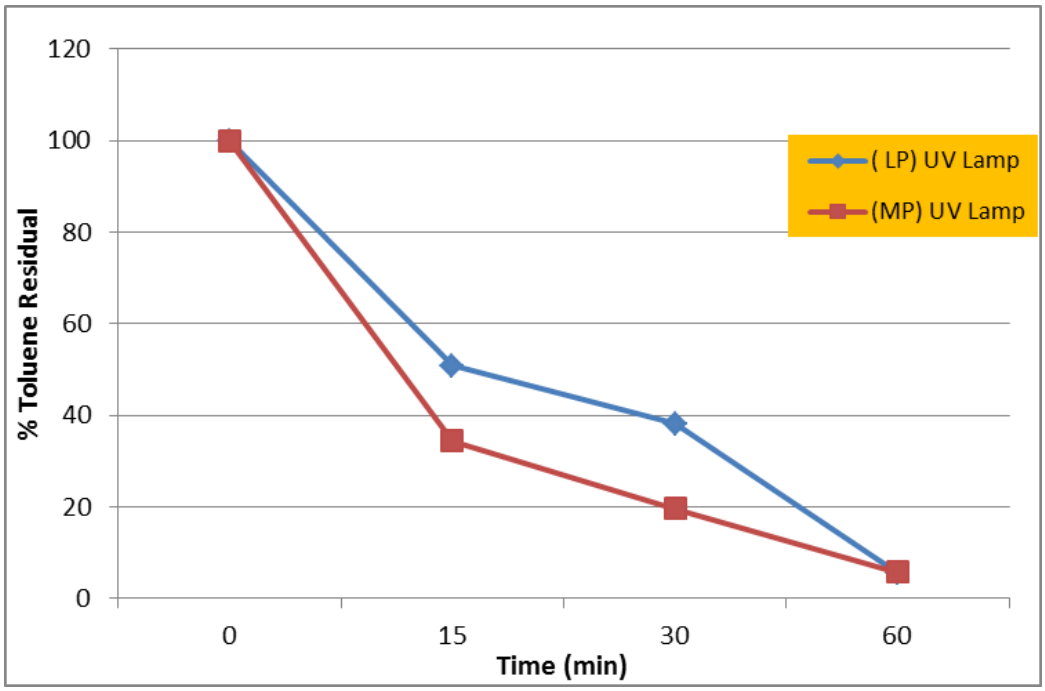

Figure 14. Residual toluene analyzed by GC-MS after treatment with (LP, MP) UV lamps, 10 ppm initial toluene concentration, and 60 minutes contact time.

Benzaldehyde was detected in both experiments of Figure 14. The benzaldehyde has a chromophore consisting of C=O bonds, which has a higher absorbance than the C-C bond of toluene. By screening the benzaldehyde spectrum using a UV-Vis spectrophotometer with the same initial concentration of toluene (10 ppm) at the same wavelength range of 220-500 nm, benzaldehyde showed much greater absorbance than toluene, with results shown in Figure 15. This observation can confirm the removal of toluene and explain the absorbance of the formed by-products, in this case apparently benzaldehyde.

Further investigations were conducted to compare toluene and benzaldehyde absorbance at same wavelength (toluene λ_{max} 262 nm). Two solutions prepared of 1 ppm of toluene and 1 ppm of benzaldehyde. The absorbances of these solutions were 0.0114 and 0.4201, respectively. This indicates that benzaldehyde absorbs 37 fold higher than toluene at the same range. Results are shown in Figure 16.

In summary, from the results obtained from Figures 13-16, it can be concluded that the high absorbance is not surprising given that the the formed by-product is benzaldehyde. As described in another report, irradiation of toluene results in benzaldehyde as the main by-product [42].

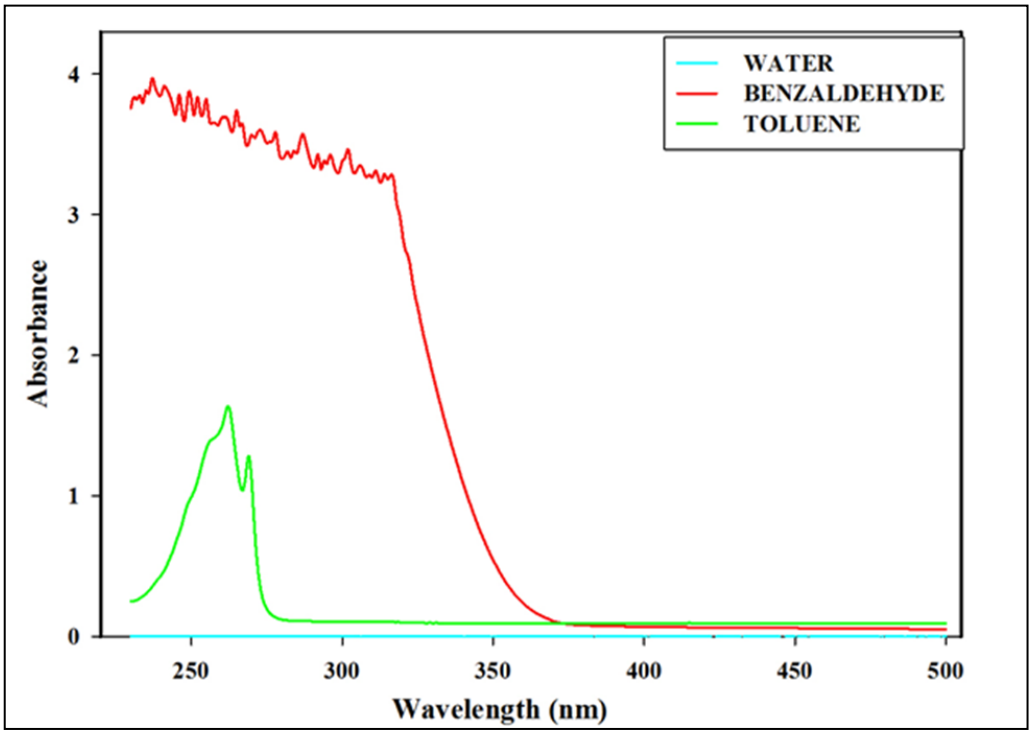

Figure 15. Benzaldehyde and toluene UV spectra [220–500 nm]

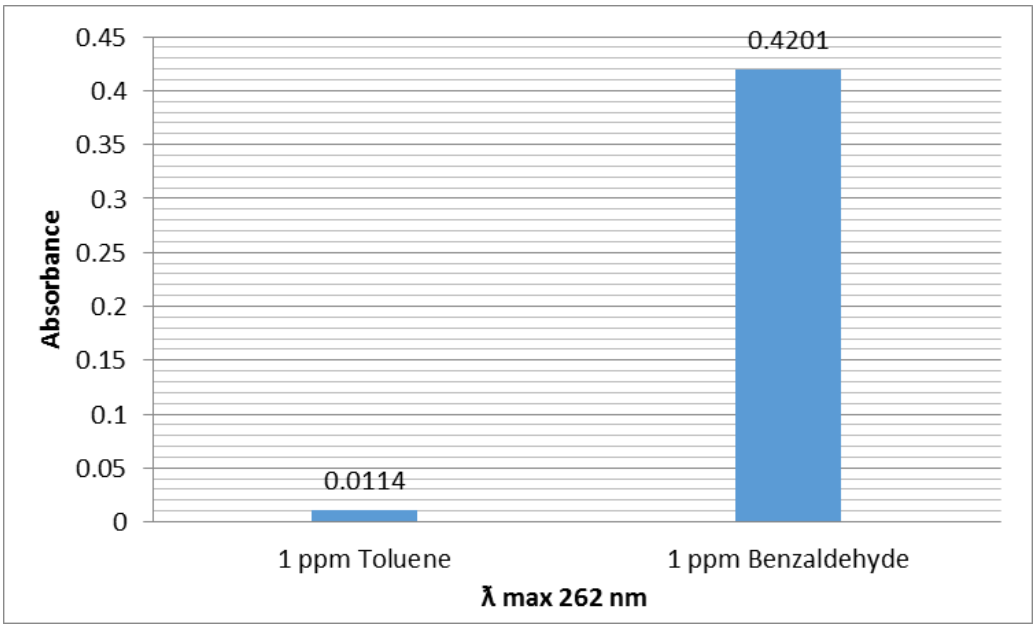

Figure 16. UV-VIS Spectrometer absorbance [262 nm] for benzaldehyde and toluene at 1 ppm

4.1.4 Degradation of Benzaldehyde by UV Alone

Further experiments were carried out by exposing a benzaldehyde solution of 10 ppm in the photoreactor to a LP UV lamp (15 Watt). The results showed that benzaldehyde was stable for 75 minutes and then started to decline slowly to reach 97% after 120 minutes. In conclusion, there was no significant loss, as shown in Figure 17. The reason for this could be attributed to lack of OH• radical generation by UV in the absence of H_2O_2 [43]. Previous studies involving the use of UV alone and UV/H_2O_2 reported similar observations regarding the treatment of other organic compounds, including (metol) N-methyl-p-aminophenol [44], hydroxyl phenyl acetic acid [45], benzothiazole and its derivatives [43], and MTBE [46]. Photolysis of benzaldehyde has been reported with a maximum occurrence in the wavelength range of 280-308 nm [47]. A low pressure (LP) lamp used emits radiation at a wavelength of 245 nm with an intensity of 15 Watts and a medium pressure lamp (MP) that delivers a broadband spectrum over the complete range of 200-300 nm with intensity of 150 Watts were both used in these experiments.

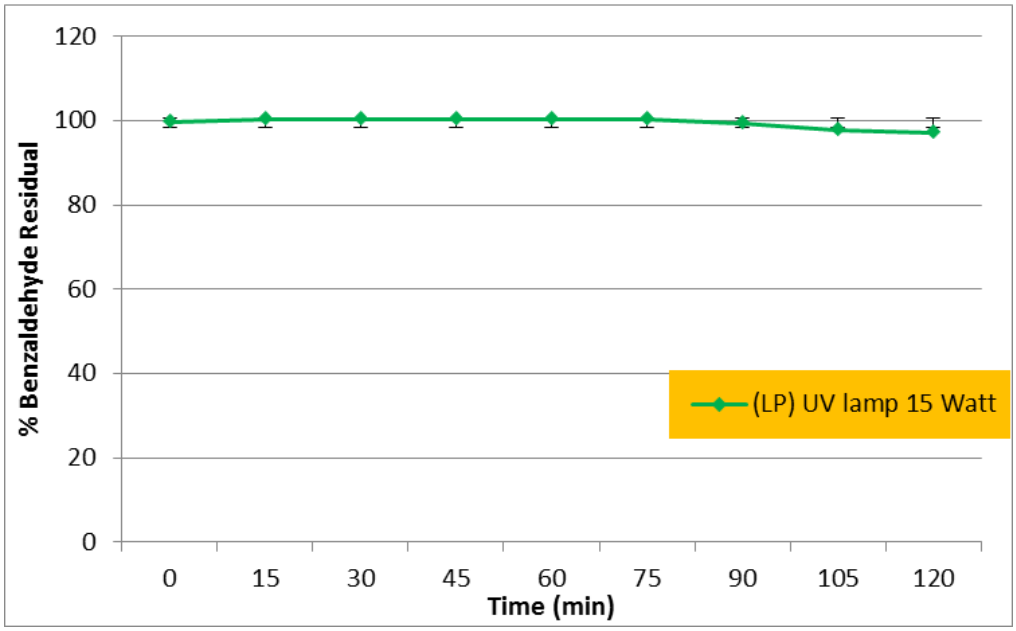

Figure 17. Residual benzaldehyde after treatment with a LP UV lamp, 10 ppm initial benzaldehyde concentration

4.1.5 Removal of Toluene by the UV-H_2O_2 Process

A set of experiments were carried out to investigate the efficiency of the UV-H_2O_2 process for the removal of toluene, combined with a 15 Watt low pressure (LP) UV lamp having an intensity of $6*10^{-3}$ mW/cm^2 and by a 150 Watt medium pressure (MP) UV lamp with a light intensity of $5.3*10^{-2}$ W/cm^2. Both lamps were combined with 100 ppm hydrogen peroxide. Water samples containing 10 ppm toluene were exposed to the UV-H_2O_2 treatment. Water samples were collected over the course of a 60 minutes treatment and analyzed.

Results were obtained using a UV-Vis spectrophotometer for the combined toluene and residual by-products. While GC-MS results were obtained for determination of residual toluene concentration.

These results using a LP UV lamp run are given in Figure 18. The UV-VIS Spectrophotometer results showed that 20.7% residual exists after 60 min versus 8% at 5 min and 0% at 10 min, as measured by GC-MS and revealed in Figure 18.

For a MP UV lamp run, the UV-VIS spectrophotometry results showed 7.5% reduction for toluene and by-products residual after 60 min versus 1.7% at 5 min and 0% at 10 min, as measured by GC-MS for Toluene residual and shown in Figure 19.

These results show better performance than many previously reported toluene treatments by AOP. The O_3-PCO, UV/O_3 and O_3/TiO_2 treatments were 96% , 89.5%, and 86.5% at 30 minutes, respectively [20]. Another study regarding removal of

toluene from the gaseous phase by UV/ TiO_2 reported a high removal of 52% in 6 hours [38]. However, since the MP UV lamp did not show the significance removal obtained from treatment with a LP. The following experiments were conducted by a LP UV lamp since it represents more feasibilities and is economically more efficient from an energy consumption perspective, as Figure 20 demonstrates.

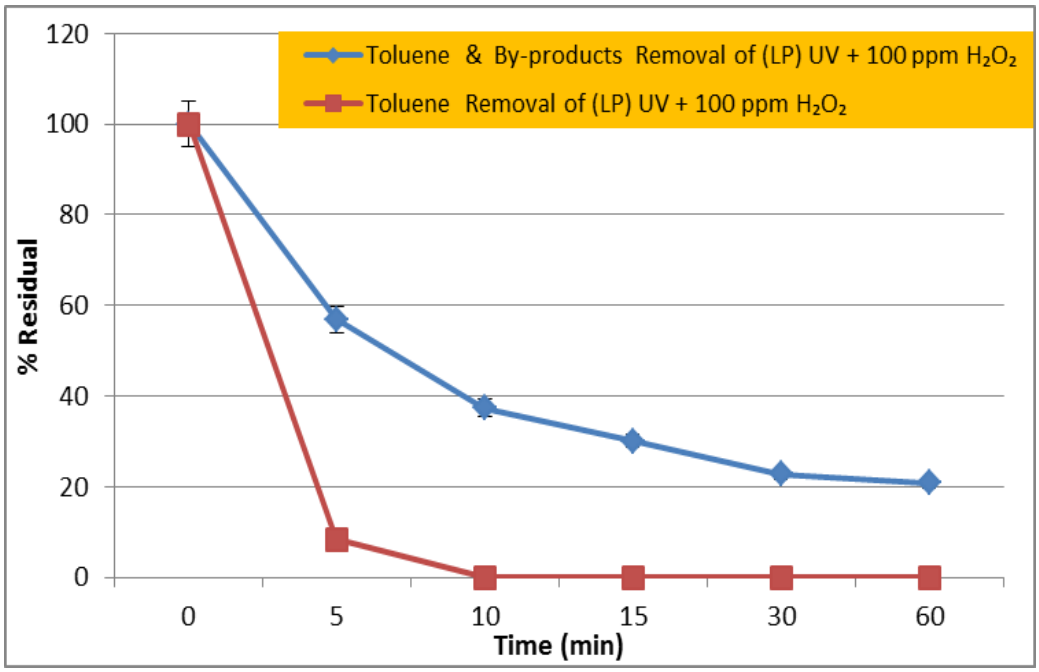

Figure 18. Residual toluene and by-products from treatment using a LP UV lamp with 100 ppm H_2O_2, 10 ppm initial toluene concentration by UV-Vis and GC-MS. Both are after 60 minutes contact time.

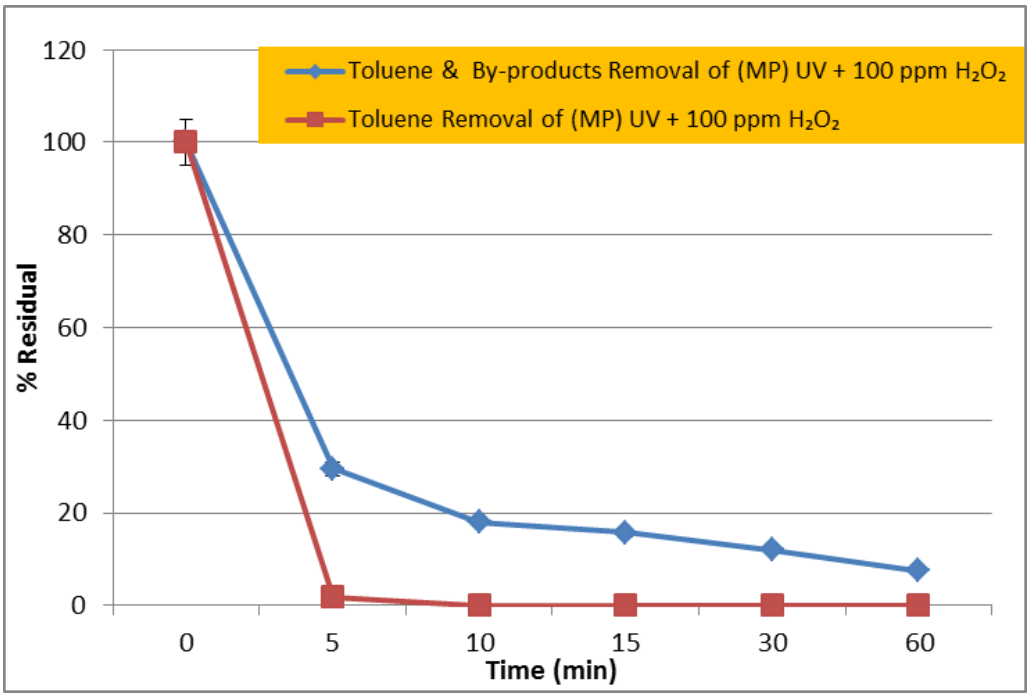

Figure 19. Residual toluene and by-products from treatment using a MP UV lamp with 100 ppm H_2O_2, 10 ppm initial toluene concentration by UV-VIS and GC-MS.

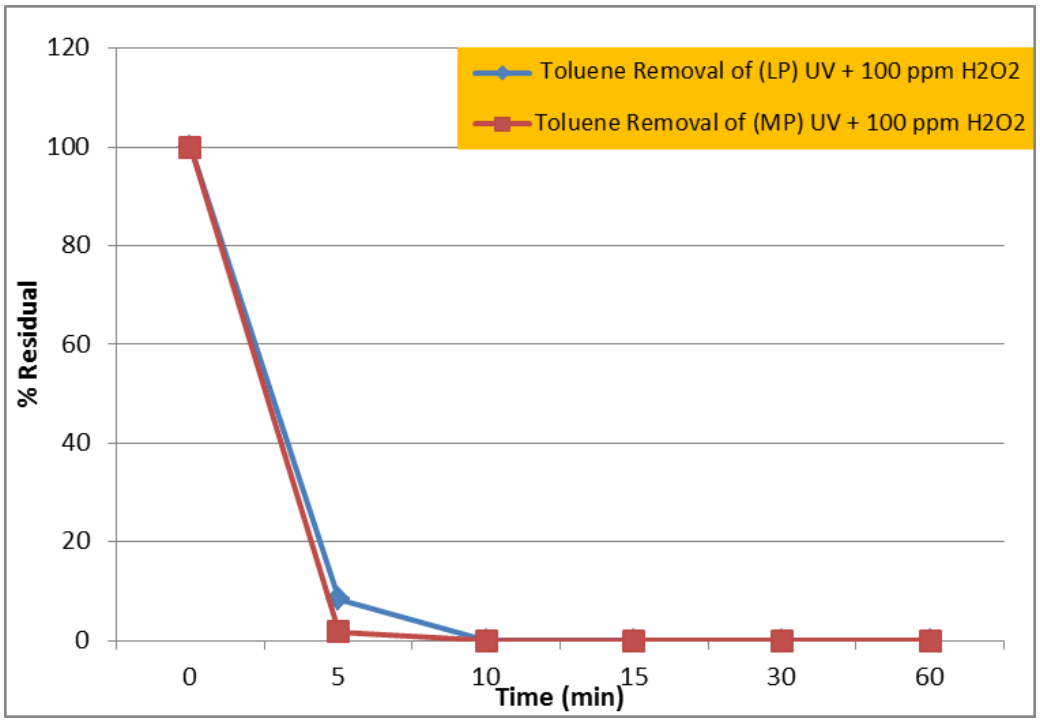

Figure 20. Residual toluene residual by GC-MS after treatment using LP and MP UV lamps with 100 ppm H_2O_2, 10 ppm initial toluene concentration, and 60 minutes contact time.

The GC-MS scanning mode in both of the previous experiments (Figure 20) was able to detect benzaldehyde within the sample collected and, according the benzaldehyde absorbance details obtained from sections (4.1.3) and (4.1.4) (Figures 15-17), the difference between the GC-MS and UV-VIS spectra results can be explained by the high absorbance of benzaldehyde. Benzaldehyde has been previously proposed as the major by-product of toluene degradation [20].

However, the increased readings seen in the UV-VIS spectrophotometer were not observed in UV-H_2O_2 treatment process, unlike UV irradiation alone treatment for toluene, which could be due to the hydroxyl radicals generated from H_2O_2 when exposed to UV irradiation. These radicals quickly attack the organic compound of toluene and its by-products, such as benzaldehyde, that cause high absorbance reading when formed in the water.

UV-H_2O_2 treatment appears to occur through a different mechanism from UV alone, which can be referred to as photolysis. Another experiment was conducted to confirm this conclusion by exposing benzaldehyde at 10 ppm to the LP UV-H_2O_2 treatment process, as shown in Figure 21.

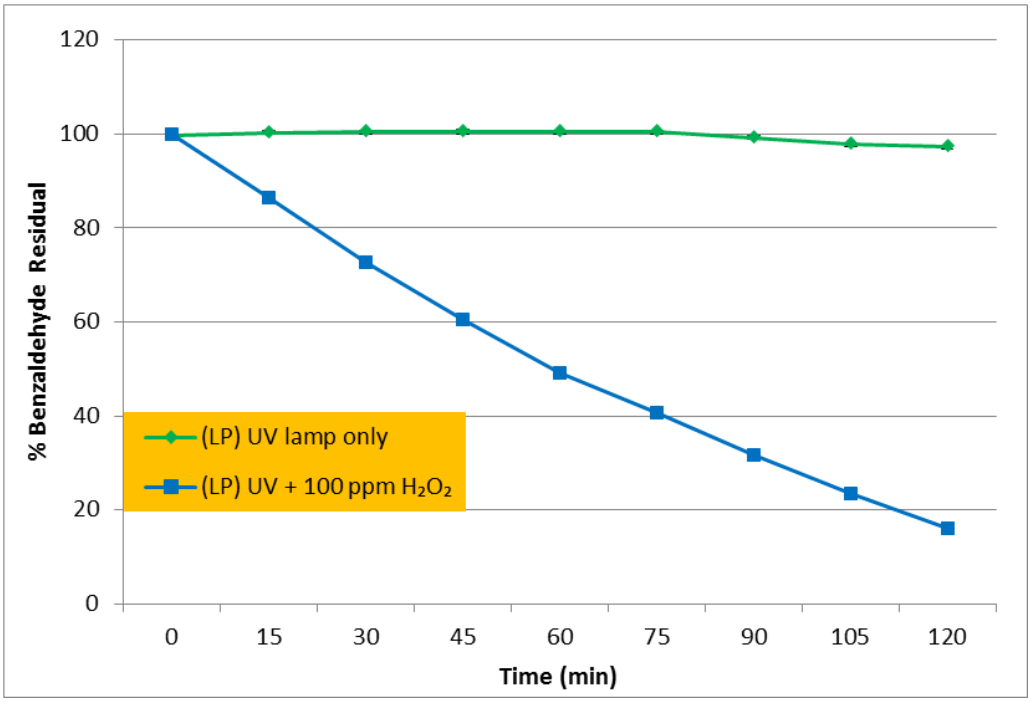

Figure 21. Residual benzaldehyde after treatment using a LP UV-H_2O_2, 10 ppm initial benzaldehyde concentration.

Benzaldehyde is colorless liquid with an almond-like odor. It is used in the food industry for flavoring and in the cosmetics industry for fragrance. The solubility of benzaldehyde in water is 3.5798 g/L at 20 ºC. USEPA has classified benzaldehyde as hazardous at high concentrations and with prolonged exposure. It recommends limiting the human daily exposure to 15mg/day. This is the Acceptable Daily Intake (ADI) [30].

Benzaldehyde is denser than water. Because it can sink in water, it moves rapidly through soil to reach groundwater sources in the case of spills. The Drinking Water MCL for toluene is 1 ppm, as proposed by the US EPA. However, there is no MCL regulation for benzaldehyde concentration in water because it is not considered a serious pollutant [12].

Although benzaldehyde is absorbed through the skin and lungs, it completely metabolizes and passes out of the body without accumulation in any human tissues [48]. Even though it has not been implicated in reproductive repercussions or as carcinogenic, it has been documented as a mutagen [49]. This implies that care must be taken while handing this chemical. Chemically, it is incompatible with most oxidizing agents. However, at low concentration, it paradoxically rapidly oxidizes to benzoic acid [50].

In summary, it is concluded that using UV/H_2O_2 for photo-degradation of toluene converts toluene to benzaldehyde [42]. The concentration of the benzaldehyde produced is very low, but it shows higher peaks in UV-Vis spectra than in GC-MS. That is why the readings consistently gives false higher concentrations of toluene by UV-Vis. Synchronically, benzaldehyde is oxidized as well [31], [50]. Therefore, the

apparent concentrations of toluene and benzaldehyde come down with time through exposure to the UV/H_2O_2 process, according the GC-MS results .

Another experiment was conducted to assess toluene treatment by UV-H_2O_2. The results are depicted in Figure 22 and show the degradation of toluene and the formation of benzaldehyde. Both are detected by GC-MS within same samples collected from Figure 22. The results showed that toluene has been reduced from 10 to 0.86 ppm after 10 minutes of treatment, equivalent to a 91% removal. When, after 15 minutes, it reached 0.27 ppm, that is equivalent to a 97% removal. Moreover, Figure 22 shows the formation of benzaldehyde coupled to toluene degradation. From the same figure, the concentration of benzeldehyde increased to approximately 0.34 ppm in the first 2 minutes, after which it begins to slightly decrease to approximately 0.07 ppm after 30 minutes. Previous research has also demonstrated formation of benzaldehyde when toluene is oxidized, especially in the presence of water [38], [51]. Furthermore, regarding the removal rate of toluene, the same figure shows that the rate decreased as the by-product (benzaldehyde) formation increases. Similar observations were reported by Bianchi et al. [52], which demonstrated a decrease in toluene treatment rates because of the formation of more than one by-products. In that report the observation was attributed to the photoactive sites facing competitiveness with oxidative agent exposure.

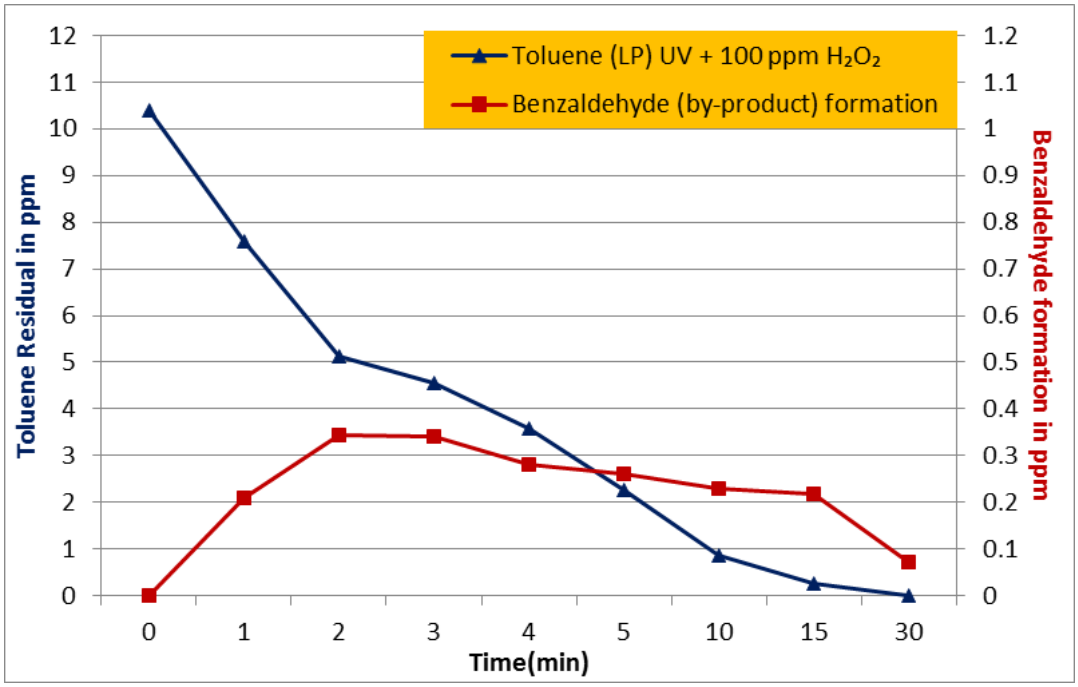

Figure 22. Residual toluene levels analyzed by GC-MS after treatment using a LP UV lamp with 100 ppm H_2O_2, 10 ppm initial toluene concentration, and 30 minutes contact time. Benzaldehyde formation was quantified by GC-MS from the same samples.

4.2 Optimal Conditions to degrade Toluene & By-products

Experiments on the optimal conditions were selected for LP UV–H_2O_2 based on the following criteria:

1. The pH level
2. Hydrogen Peroxide (H_2O_2) concentration
3. Initial toluene concentration
4. Contact time

Based on the above evaluation criteria, an improved degradation performance of toluene and by-products in water was examined under LP UV–H_2O_2 and this information is shown within the next sub-sections of experiments results.

4.2.1 Effect of pH on degradation of toluene & by-products

The pH effects were examined via several experiments involving different pH level of 9, 7, and 4 with the LP UV-H_2O_2 process and an initial toluene concentration of 10 ppm spiked in DIW, after adjusting the water pH by adding 0.1 M acetic acid and 0.1 M Na_2CO_3 to reach the required pH. Samples were collected at different time intervals over 60 minutes and analyzed by UV-VIS spectrophotometry. The results are depicted in Figure 23.

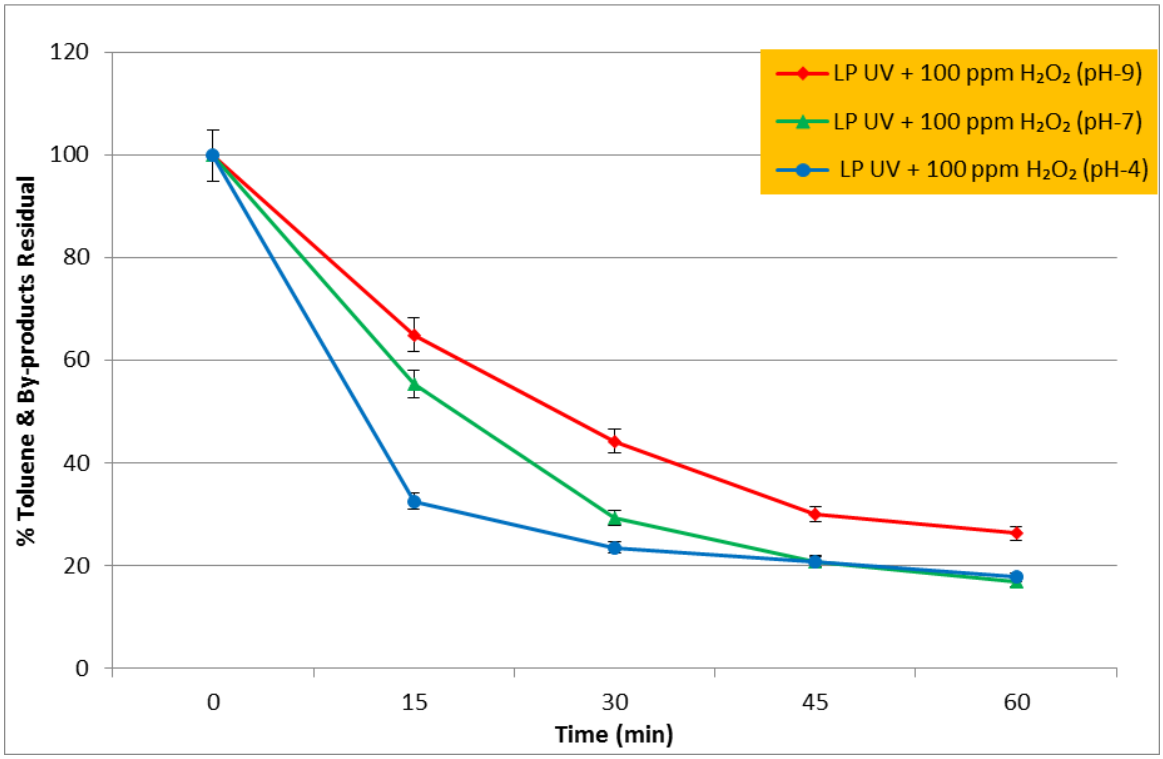

Figure 23. Residual toluene and by-products from treatment using a LP UV lamp with 100 ppm H_2O_2, 10 ppm initial toluene concentration, and pH 9, 7, and 4 by UV-VIS

Figure 23 shows the effects of pH values on the treatment of toluene in the presence of 100 ppm H_2O_2 and LP UV radiation. The figure shows that toluene treatment is faster in an acidic medium (pH 4) and slows down considerably as the pH value increases. Although the final concentration of toluene after 60 minutes of treatment is similar at both pH 4 and 7, the reaction is faster at pH 4. In contrast, the reaction is a little slower and has poorer treatment efficiency when the solution is at pH 9. This lesser performance under alkaline conditions could be attributed to the behavior of H_2O_2 at high pH values. H_2O_2 decomposes rapidly in basic medium and thus has a low residence time, which does not allow efficient generation of $OH^{\bullet}$ radical for the degradation of toluene. Similar results have been reported with MTBE [46], as well as benzoic acid and phenol [53]. In addition, applied artificial neural network (ANN) modeling has predicted similar pH–UV/H_2O_2 photo-degradation behavior for some organic contaminants (including toluene) in the wastewater reported by Vaferi et al. [28].

4.2.2 Effect of H_2O_2 dose on degradation of toluene & by-products

The effect of hydrogen peroxide doses was investigated through the addition different dosage of H_2O_2 (50, 100, and 200 ppm) to the 10 ppm toluene spiked DIW. The solution was then exposed to the UV-H_2O_2 process and samples collected at different contact time intervals during 60 minutes and analyzed by UV-VIS spectrophotometry.

The concentration of 100 ppm showed the best degradation, as per Figure 24. This can be explained through the assumption that the 50 ppm of H_2O_2 dose was not generating enough radicals to effectively attack toluene and its by-products. For the case at the higher dose of 200 ppm, H_2O_2 results were also less efficient than at 100 ppm H_2O_2, but in this case it is due to excess the H_2O_2 concentration acting as radical scavengers and increasing the competition between toluene and its by-products and the excess H_2O_2. Figure 24 shows the effects of H_2O_2 concentration in the treatment of toluene. As expected, the treatment rate during the first 15 minutes is similar when 50 and 100 ppm of H_2O_2 were used. The reaction slows afterwards for 50 ppm H_2O_2, implying that the generated $OH^{\bullet}$ radicals may be insufficient. Using more H_2O_2 generates additional $OH^{\bullet}$ radicals that improve treatment efficiency. This can be seen in the treatment at 100 ppm of H_2O_2. However, increasing the concentration to 200 ppm does not improve treatment efficiency. In fact, the final concentration of toluene in the case of 200 ppm H_2O_2 was slightly more than when 50 ppm of H_2O_2 was used. This is due to the fact that there is an optimal concentration of H_2O_2 that gives best treatment performance. Above that optimum, excess H_2O_2 acts as an $OH^{\bullet}$ scavenger [54] and quenches the formation of further $OH^{\bullet}$ radicals, resulting in reducing the available $OH^{\bullet}$ for efficient removal of toluene. Similar observations have been reported in the treatment of p-chlorophenol using UV-H_2O_2 [55], MTBE [46], Azo compounds [56], and aromatic hydrocarbons, including toluene. The observation also been explained within the two chemical reaction equations previously presented in Section 1.4, as follows:

$$H_2O_2 + h\nu \longrightarrow 2HO^{\bullet}$$

$$H_2O_2 + HO^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O$$

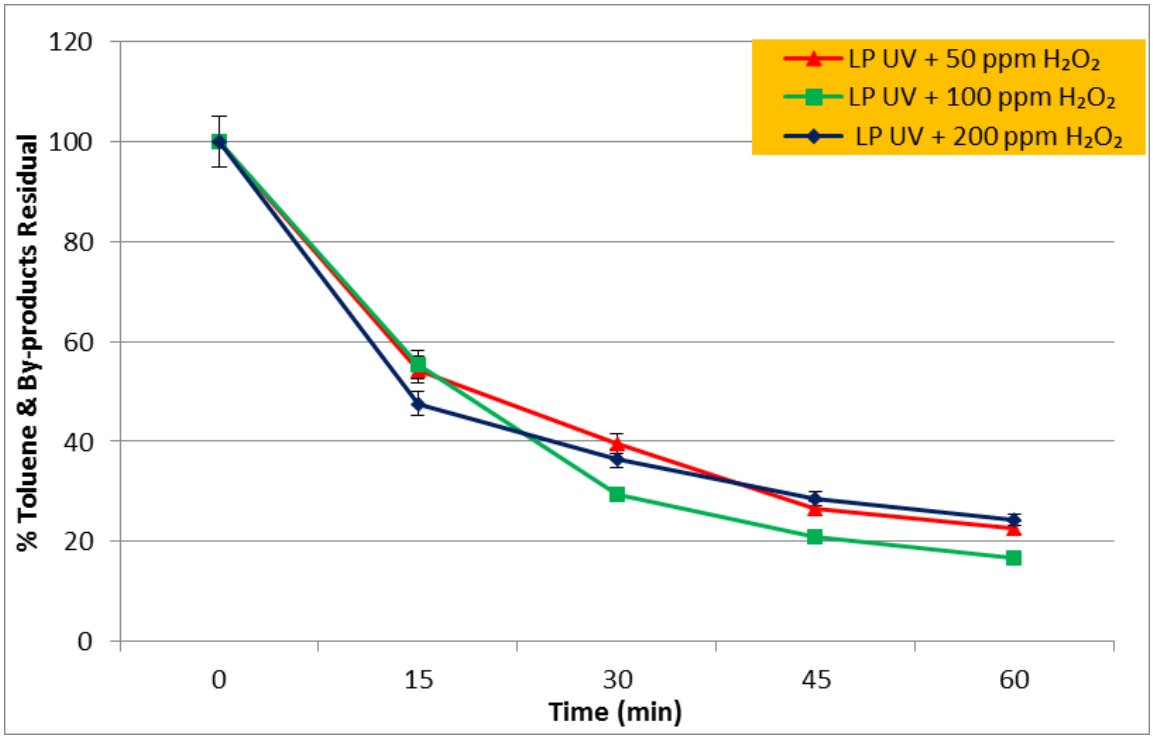

Figure 24. Residual toluene and by-products from treatment using LP UV lamp with 50, 100, or 200 ppm H_2O_2, and 10 ppm initial toluene concentration by UV-VIS. All with 60 minutes contact time.

4.2.3 Effects of toluene initial concentrations on degradation of toluene & by-products

The initial concentration factor of toluene was studied by separate experiments with DIW spiked with 5, 10, and 15 ppm initial concentrations of toluene. The different solutions were subjected to LP UV-H_2O_2 treatment with a 100 ppm of H_2O_2 dose. The samples were collected and analyzed by UV-VIS spectrophotometry at different time contact intervals. Figure 25 shows the residual toluene and by-products.

The effect of the initial toluene concentration, shown in the Figure 25, depended on the source and magnitude of contamination. The concentration of toluene in a contaminated environment would vary. Hence, initial concentration is an important factor. As shown in the figure, the higher the concentration, the lower the treatment rate. Therefore, the treatment reaction is faster with 5 ppm than the 10 and 15 ppm initial concentrations. However, the final percent of residual toluene and associated by-products are similar after 60 minutes of treatment. In previous studies involving toluene treatment by TiO_2/UV/O_3, similar observations were reported [29], [31]. At high initial toluene concentrations, more oxidants and more by-products are produced, limiting the toluene treatment rate. Advanced oxidation processes, using UV/H_2O_2 for removal of other organic compounds, also shows similar behavior. The initial concentration factor is attributed to the competition between the various target pollutant molecules and their by-products formed during the oxidative reaction process [46].

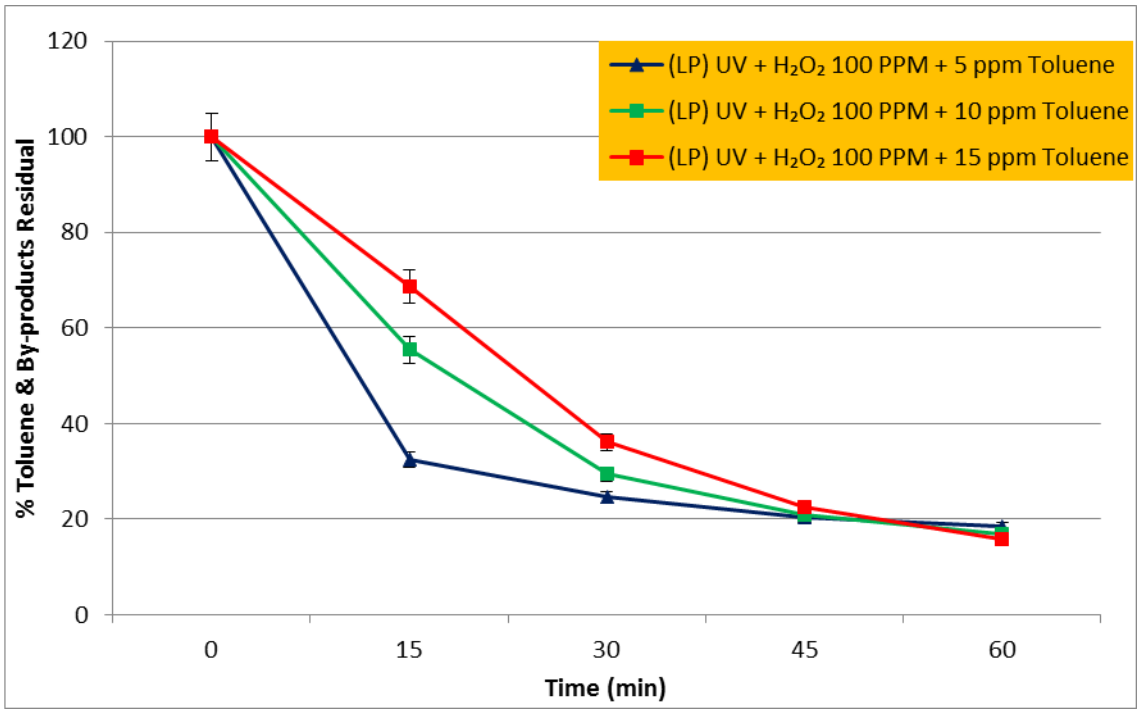

Figure 25. Residual toluene and by-products from treatment using a LP UV lamp with 100 ppm H_2O_2, and 5, 10, or 15 ppm initial toluene concentration and measured by UV-VIS. All with 60 minutes contact time.

4.2.4 Results for optimal conditions

From the previous experiments of sub-sections of 4.2 (Figures 23-25), the best results for toluene and its by-products are obtained with the following conditions:

- pH 4 showing improved treatment, compared to pH 7 and 9
- H_2O_2 concentration of 100 ppm was slightly better for 10 ppm toluene treatment than 50 and 200 ppm dosages of H_2O_2
- Toluene initial concentration of 5 ppm performed better than 15 and 10 ppm toluene concentration when exposed to LP UV. Lower concentrations showed better removal rates

This information was obtained for DIW, and for salinity (TDS) effects. Further elucidation of the optimal treatment for ground water (GW) by additional experiments are shown in section 4.3.

4.3 Removal of toluene from spiked Dhahran groundwater

The same conditions obtained from the synthetic water experiments were tested for real groundwater (GW) collected from King Fahad University of Petroleum & Minerals (KFUPM) well number 9 (next to building 26). The GW was tested for its ionic and trace metals composition using Metrohm 850 Professional Ion Chromatography (Magic Net IC) and an Optima 8000 ICP-OES Spectrometer (Perkin Elmer®), respectively. The results are shown in Table 5.

Table 5. Groundwater Characterization Analysis

Parameters	Unit	Mean	Std Dev
pH	-	7.35	0.26
TDS	ppm	5368.22	247.73
Conductivity	µS/cm	2843.00	11.15
Na	mg/L	793.65	2.91
K	mg/L	25.3	0.71
Ca	mg/L	493.90	3.21
Mg	mg/L	130.20	0.63
F	mg/L	0.47	0.09
Cl	mg/L	1468.43	4.77
Br	mg/L	62.65	1.24
NO_3	mg/L	1.38	0.05
SO_4	mg/L	572.35	1.68
Sr	mg/L	7.4	
Ni	mg/L	ND	
Fe	mg/L	ND	

The optimal conditions obtained from DIW for removal of toluene were tested with GW. The following experiments were conducted to investigate the effect of salinity on the efficiency of treatment using the UV-H_2O_2 process for real GW. The GW has a TDS of approximately 5000 ppm. Three levels of TDS have been tested by diluting the GW into 2500 and 1250 ppm. The three TDS levels were exposed to LP UV-H_2O_2 processes with 100 ppm H_2O_2 at a pH of 4. Samples were collected over 60 minutes and analyzed for residual toluene by GC-MS.

It was found that the LP UV and 100 ppm of H_2O_2 was the most efficient at degrading toluene in GW, with a >99% removal efficiency for toluene that occurred after 30 minutes at the three TDS levels. However, the three TDS levels had different removal rates at 15 minutes of contact time. The GW of TDS (5000, 2500 and 1250 ppm) had removal rate of 67%, 77%, and 89%, respectively according Figure 26. Comparing these results with the DIW results obtained from Figure 22, the removal efficiency in DIW was 97% at 15 minutes. The difference in removal rate between DIW and GW can be attributed to the high salinity in the treated GW. Tawabini et al. [57] reported that alkalinity and ions, such as sulfate, bromide, and nitrate, act as scavengers for $OH^{\bullet}$ radicals and thus limit UV/H_2O_2 treatment performance.

It can be concluded that as salinity concentration increases, the removal efficiency of toluene decreases. This is due to the existence of scavengers (i.e. cations and anions). Even though the final concentrations after 30 minutes of contact time are similar for all the TDS levels, pretreatment of dissolved solids could be required to reduce treatment time and thus save electrical energy. Li et al. [36] reported the importance of pretreatment in the application of UV/H_2O_2 for treatment of organic contaminants to save energy and time [36]. Fig. 26 shows the GW results for different concentrations, compared to (Figure 22) DIW results after 15 minutes treatments from initial concentration of 10 ppm toluene to demonstrate the efficiency of reaction.

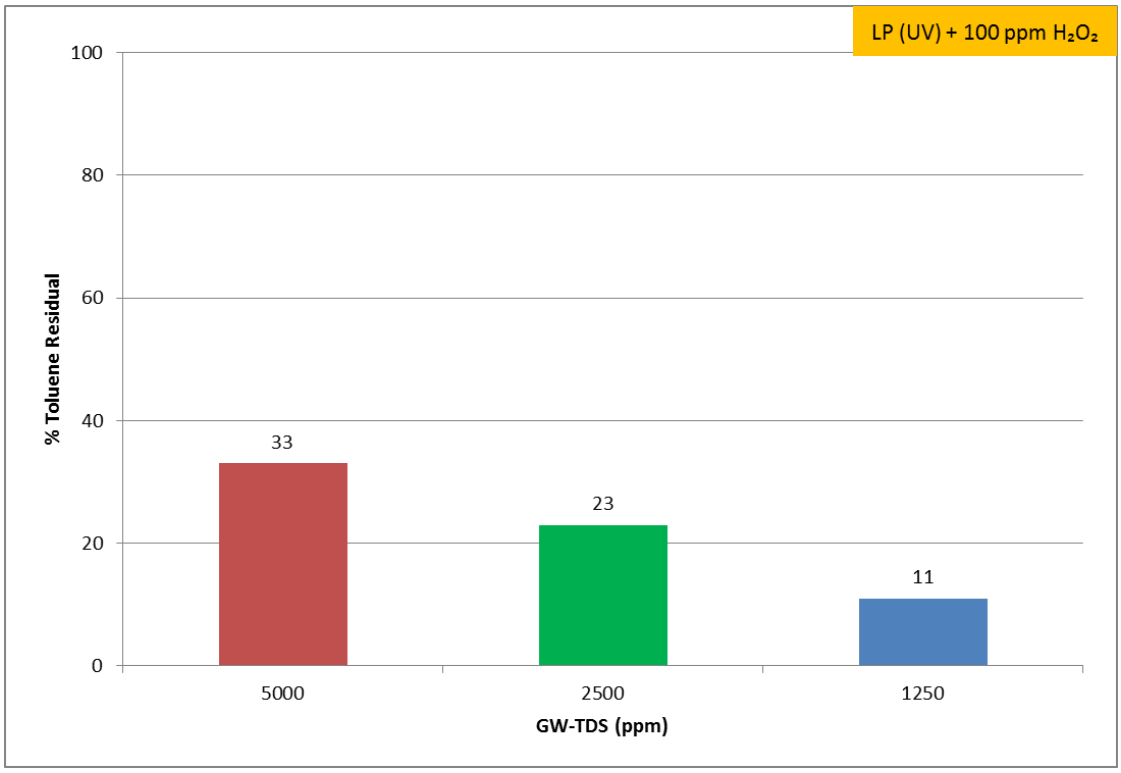

Figure 26. Residual toluene from treatment using a LP UV lamp with 100 ppm H_2O_2, 10 ppm initial toluene concentration, at pH 4, as measured by GC-MS after 15 minutes contact time for GW (5000, 2500, and 1250 TDS)

4.4 Kinetic studies of toluene degradation

4.4.1 Degradation of toluene by UV Irradiation alone

The kinetics of toluene removal in the photoreactor was studied for both the 15 Watts low pressure (LP) UV lamp with an intensity of $6*10^{-3}$ mW/cm^2, and for the 150 Watts medium pressure (MP) UV lamp with a light intensity of $5.3*10^{-2}$ W/cm^2. From the results obtained, it is clear that the removal of toluene by LP UV can be represented by first order reaction kinetics.

Using the removal data of toluene demonstrated in Figure 14, a semi-logarithmic plot of (-lin $C/C_{\circ}$) was created, as shown in Figure 27. It can be concluded from Figure 27 that toluene removal by a 15 Watts LP UV lamp follows first order kinetics with a rate constant (k) equal to 0.048 and $R^2 = 0.96$.

Similarly, a semi-log plot of toluene removal by a 150 Watts MP UV was created, as shown in Figure 28. The data was extracted from Figure 14. It can be concluded from Figure 28, that toluene removal by a MP UV lamp follows first order kinetics with a rate constant k equal to 0.0442 with $R^2 = 0.97$.

From the above results, the rates of the degradation for toluene by the two types of UV lamps are similar. This indicates that the photolysis rate of toluene by LP and MP were not very different.

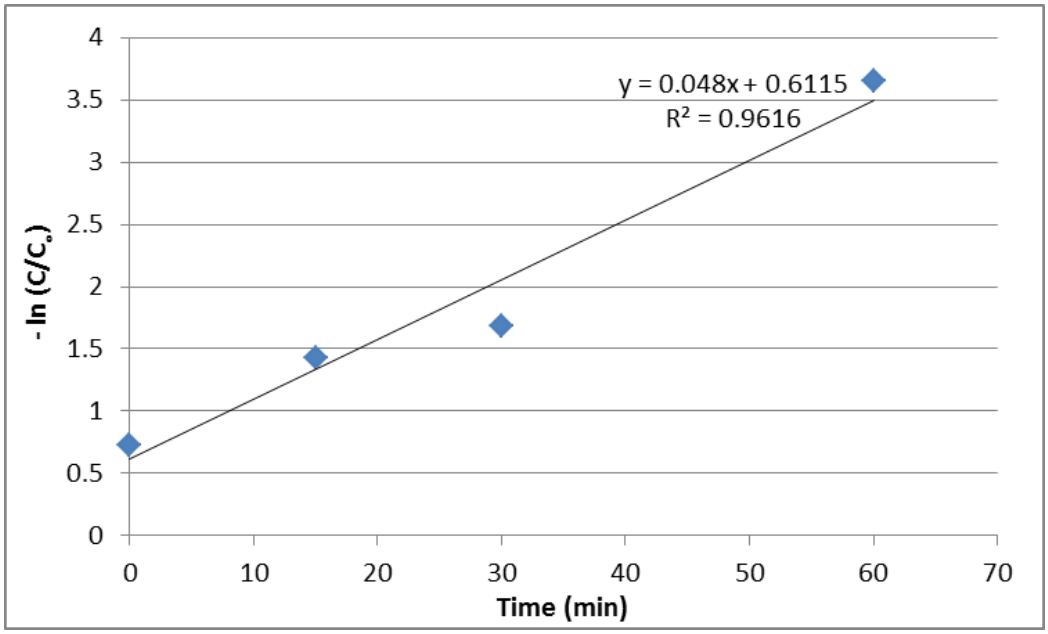

Figure 27. First order kinetic model fit of toluene degradation by LP UV

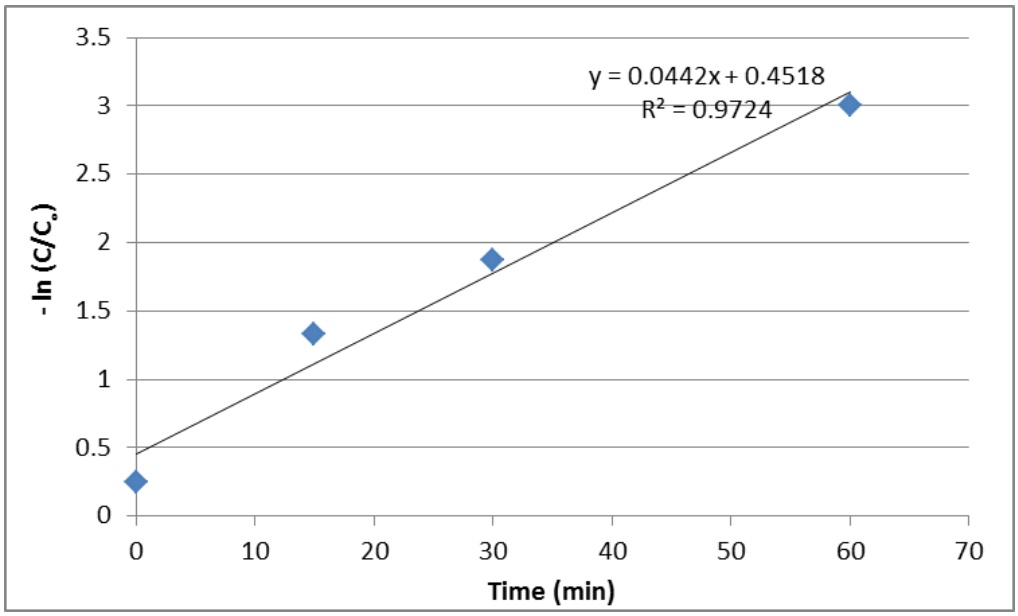

Figure 28. First order kinetic model fit of toluene degradation by MP UV

4.4.2 Degradation of toluene by UV-H_2O_2

The kinetics of toluene removal were also studied under the same conditions as the Figure 22 experiment using the LP UV-H_2O_2 process. The degradation rate of toluene under these experimental conditions was extremely rapid and, because of that, samples were collected every minute for the first 5 minutes. For kinetics studies, this was the best available approach to the current photoreactor system, which has limitations on collecting samples at intervals less than 1 minute. Figure 29 shows the results obtained for DIW using the semi-log plot presented in Figure 22 for toluene removal by the LP UV-H_2O_2 process. The results follow first order kinetics with R^2= 0.92 and a removal rate of k = 0.3593. The results also show the k value for the toluene:H_2O_2 ratio of 1:10.

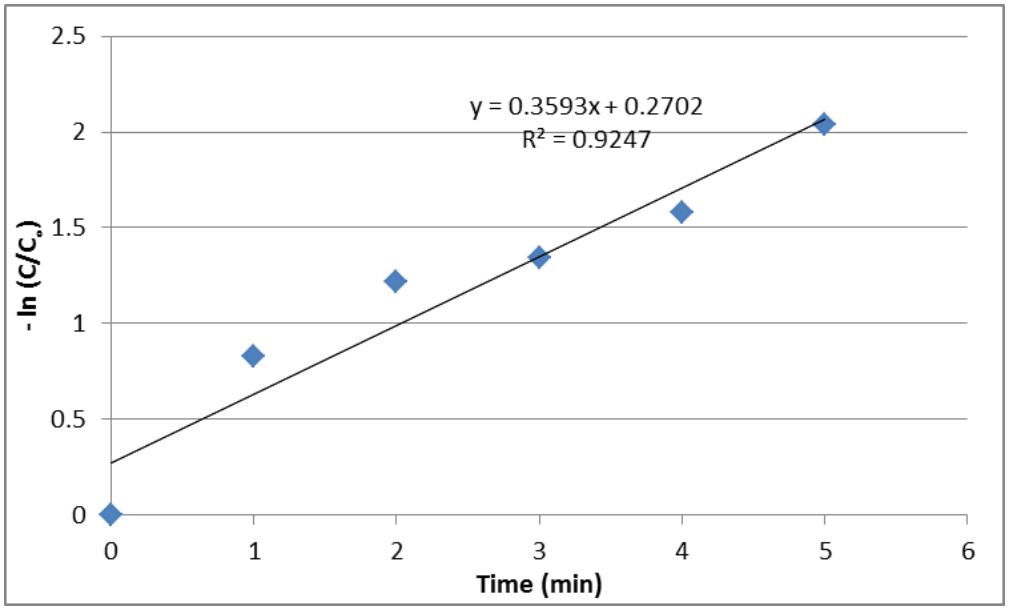

Figure 29. First order kinetic model fit of toluene degradation by LP UV, with 100 ppm H_2O_2, for the first 5 minute intervals samples.

4.5 Estimation of electrical energy per order (EE/O)

In this study, the energy consumed to degrade toluene in distilled and groundwater was estimated for the experiments results obtained from sections 4.1.5 and 4.3 (Figures 22, 26), both on the bench scale for DIW and GW. The electrical energy per order (required energy per 1 order of removal) was calculated for the LP UV treatment with 100 ppm H_2O_2 to treat 90% of 10 ppm Toluene. The EE/O for DIW (10 min, 91.74% removal) and for GW is (30 min, >99% removal) are equivalent to UV doses of 4.8 and 15 kWh/m^3, respectively, as shown in Table 6. The table has illustrations of initial concentration (C_i) and final concentration (C_f) for each time interval.

Table 6. EE/O and UV dose for DIW and GW treatment using LP UV-H_2O_2

Treatment	Matrix	Time(min)	Time(hr)	p (Kw)	V (m3)	Toluene Ci (ppm)	Toluene Cf (ppm)	UV dose (kWh/m^3) = p(kW)*t(hr)/V(m^3)
LP UV + 100 ppm H_2O_2	DIW	0	0	0.015	0.0005	10.4	10.4	**0**
		1	0.01	0.015	0.0005	10.4	7.6	**0.3**
		2	0.03	0.015	0.0005	10.4	5.13	**0.9**
		3	0.05	0.015	0.0005	10.4	4.55	**1.5**
		4	0.06	0.015	0.0005	10.4	3.59	**1.8**
		5	0.08	0.015	0.0005	10.4	2.26	**2.4**
		10	0.16	0.015	0.0005	10.4	0.86	**4.8**
		15	0.25	0.015	0.0005	10.4	0.27	**7.5**
		30	0.5	0.015	0.0005	10.4	0.01	**15**
	GW	0	0	0.015	0.0005	10.2	10.2	**0**
		15	0.25	0.015	0.0005	10.2	3.43	**7.5**
		30	0.5	0.015	0.0005	10.2	0.01	**15**

4.6 Cost estimation for degradation of toluene with UV irradiation and H_2O_2

The conditions of the removal of toluene using LP UV lamp with 100 ppm H_2O_2 from DIW and GW were investigated, specifically the experimental results obtained from sections 4.1.5 and 4.3 (Figures 22, 26) and their electrical energy per order (EE/O) calculated in section 4.5 Table 7. The semi-logarithmic plot of DIW results, shown in Figure 30, which indicate the time required for reducing the concentration of toluene by an order of magnitude is 10 minutes. This was used as the cost estimation and, as per the GW data; the time calculated for cost estimations is 30 minutes.

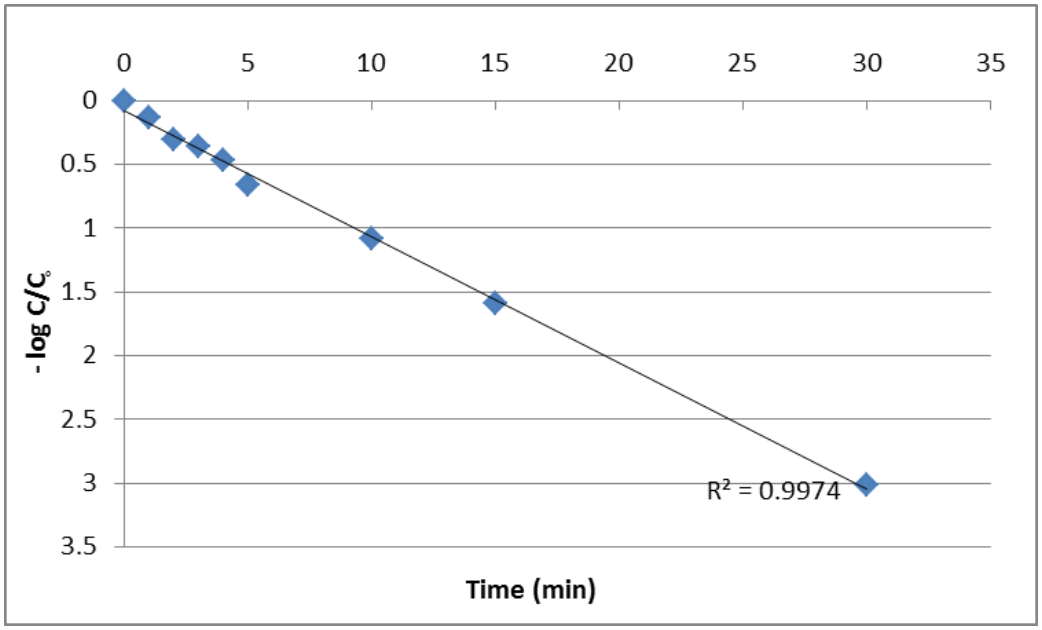

Figure 30. DIW Semi-logarithmic plot of toluene degradation by LP UV lamp (15 Watts) and 100 ppm H_2O_2

The following Table 7 shows the calculations used to determine the estimated cost value for toluene removal by UV-H_2O_2 at the 10 minute time selected, with the EE/O value of 4.8 kWh/m^3 for DIW. The cost estimated for GW was calculated for 30 minutes and with the EE/O value of 15 kWh/m^3.

Once the UV dose has been calculated, the operating cost of the UV-H_2O_2 treatment can be estimated using the following equation:

Operating Cost / m^3 = [EE/O * log(Ci/Cf) * Electrical cost * 1.35] + H_2O_2 cost [58].

In this study the estimated operating cost (in SR) of AOP to treat 1 m^3 of contaminated DIW and GW were calculated as follows:

1- The average electrical charges for commercial use is 0.3 SR/kWh, according to Saudi Electricity Company tariffs.

2- The cost of H_2O_2

- Optimum concentration of H_2O_2 = 100 ppm for a 10 ppm initial toluene concentration
- Approximate cost of 30% H_2O_2 solution = 3 SR/L
- Volume of 30% H_2O_2 added to 0.5 L reactor to reach 100 ppm = 151 µL, or

  302 mL/m^3
- Cost of adding 0.3 L H_2O_2 = 1 SR/m^3

3- Operating cost = [EE/O * log(Ci/Cf) * Electrical cost * 1.35]+ H_2O_2 cost

= 3.1 SR/m^3 for DIW at 10 min (1 order of magnitude removal), and

= 19.2 SR /m^3 for GW at 30 min (complete removal)

In addition to the data obtained from Figure 30, other costs, including capital and maintenance, should be considered during application scales.

Table 7. Cost estimation for DIW treatment with LP UV-H_2O_2

Treatment	Matrix	Time(min)	Time(hr)	p (Kw)	V (m^3)	Toluene Ci (ppm)	Toluene Cf (ppm)	Ci/Cf	log (Ci/Cf)	UV dose (kWh/m^3) = p(kW)*t(hr)/V(m^3)	Operating Cost / m^3 = [EE/O * log(Ci/Cf) * Electrical cost * 1.35] + H_2O_2 cost
LP UV + 100 ppm H_2O_2	DIW	0	0	0.015	0.0005	10.4	10.4	1	0	**0**	1.0
		1	0.01	0.015	0.0005	10.4	7.6	1.36842	0.13622	**0.3**	1.0
		2	0.03	0.015	0.0005	10.4	5.13	2.02729	0.306916	**0.9**	1.1
		3	0.05	0.015	0.0005	10.4	4.55	2.28571	0.359022	**1.5**	1.2
		4	0.06	0.015	0.0005	10.4	3.59	2.89694	0.461939	**1.8**	1.3
		5	0.08	0.015	0.0005	10.4	2.26	4.60177	0.662925	**2.4**	1.6
		10	0.16	0.015	0.0005	10.4	0.86	12.093	1.082535	**4.8**	3.1
		15	0.25	0.015	0.0005	10.4	0.27	38.5185	1.58567	**7.5**	5.8
		30	0.5	0.015	0.0005	10.4	0.01	1040	3.017033	**15**	19.3

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The objective for this study was to investigate the efficiency of UV/H_2O_2 process to remove toluene from water under various conditions of UV type and intensity, pH, H_2O_2 dose, toluene concentration, salinity, and contact time. Moreover, the formation and removal of toluene degradation by-products (i.e. benzaldehyde) were assessed in the study. The optimum treatment conditions of toluene by UV/H_2O_2 process were: pH 4, 100 ppm H_2O_2, and 15 Watt (LP) UV lamp for removal of 10 ppm toluene in 30 minutes. These conditions were also tested for toluene-contaminated authentic groundwater samples under three (3) levels of salinity of 5000, 2500 and 1250 ppm. Results revealed that UV/H_2O_2 achieved removal rates of 67%, 77%, and 89% respectively at pH of 4 within 15 minutes contact time. The study also showed that removal of Toluene by low pressure (LP) UV source was comparable to that achieved by medium pressure (MP) lamp.

The study confirmed that Benzaldehyde was identified as the main by-product of Toluene formed by both photolysis (UV only) and UV/H_2O_2 oxidation processes. However, UV alone has low efficiency in removing the Toluene compared to the more efficient degradation by the UV/H_2O_2 process. Finally, the study showed that removal of toluene by UV/H_2O_2 process follows a first order kinetics with rate of 0.3593 and R^2 of 0.92 for Toluene:H_2O_2 ratio of 1:10.

5.2 Recommendations

Based on the findings of this study, the following recommendations are proposed:

1. Toluene removal by UV/H_2O_2 process has proven its efficiency at bench-scale level but requires to test it under pilot scale conditions.

2. Detailed analyses for by-products generated and their removal should be well investigated.

3. Other AOPs process for the removal of toluene based on ozone (i.e. UV/O_3, H_2O_2/O_3 and UV/H_2O_2/O_3) need to be investigated.

4. The effect of salinity on toluene removal by AOPs should be further investigated.

5. The cost estimation of AOPs removal technique in term of energy, chemicals, and operation need further investigation at pilot scale.

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